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Functionalisation of indene

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Dibromo- and tribromoindane were synthesised by bromination of indene. Treatment of dibromo- and tribromoindane with various silver salts (silver acetate, perchlorate, sulfate and nitrate) in different solvents opened up an entry to the synthesis of various di- and tri-substituted indane derivatives.

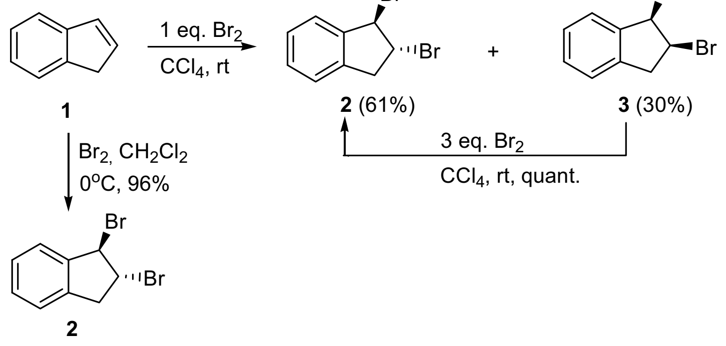
Keywords: indene, bromination, substitution

Some of the five-membered ring substituted indane derivatives show very important biological activities. For example, *cis*-1*S*,2*R*-aminoindanol is a component of the inhibitor of protease in the human immunodeficiency virus (HIV).[1] This chiral molecule can be asymmetrically synthesised from the chiral 1*S*,2*R*-indene oxide, or alternatively, from *cis*-1*S*,2*R*-indandiol or *trans*-2*S*,1*S*-bromoindanol.[2,3] Enantiomerically pure aminoindanol derivatives have recently been described as highly efficient ligands in the titanium-catalysed asymmetric Diels-Alder reaction.[4] Furthermore, a series of optically active aminoindanol derivatives was used in the catalytic enantioselective addition of diethylzinc to aldehydes.[5] Indanediols have been successfully used in the synthesis of α-hydroxyketones, which are valuable building blocks in synthetic chemistry.[6] Because of the general interest directed toward the synthesis of indane derivatives we report the bromination of indene and the conversion of bromo compounds into various indane derivatives.

The addition of bromine to indene in non-polar solvents has been found to give two major products, *trans*-1,2-dibromoindane (**2**) and *cis*-1,2-dibromoindane (**3**) in a ratio of 2:1 (Scheme 1).[7] Reaction of bromine with indene in methylene chloride at 0°C gave the *trans*-dibromide in 96% yield. Treatment of a mixture consisting of *trans*- and *cis*-dibromides **2** and **3** with 3 equivalents of bromine in daylight for 1 h revealed that the *cis*-isomer **3** was completely converted into the *trans*-isomer **2** (For spectroscopic data see Table 1).

Treatment of *trans*-1,2-dibromoindane (**2**) with 1 equivalent of silver perchlorate in aqueous acetone gave pure *trans*-2-bromoindan-1-ol (**4**)[8] in 91% yield where the configuration of the starting material is retained. Probably, the neighbouring bromine forms a cyclic bromonium ion which controls the course of substitution in this five-membered ring. A good yield (95%) of essentially pure bromoalcohol **4** was also obtained by treatment of dibromide **2** with silica gel at room temperature (Scheme 2). The treatment of the dibromide **2** with 1 equivalent of silver acetate in ether gave the monoacetate **5**[7b] with retention of configuration. The compound formal was identical with that obtained by acetylation of **4** with acetic anhydride in pyridine. The bromoacetate **5** was reacted with bromine in carbon tetrachloride while being irradiated with a 150 W projector lamp. The dibromoacetate **6** was obtained in 86% yield. The exact configuration of the formed product **6** was determined by measuring the coupling constants between the protons H_2 and H_3 (J_{23} = 3.0 Hz). Treatment of the dibromide **2** with silver sulfate in methanol yielded methoxybromoindane **7**[7d,8b] (55%) together with the oxidation product 2-bromoindan-1-one **8**[9] (25%). On the other hand, the reaction of indanedibromide **2** with silver nitrate in ether at room temperature gave rise to a *trans*-bromonitrate derivative **9**. Photochemical bromination of this product **9** resulted in the stereospecific formation of the dibromonitrate **10** with the *trans,trans* configuration.

After successful synthesis of various indane derivatives we have turned our attention to the synthesis of tribromide **11** and its derivatives (Scheme 3). The tribromide **11**[7a,10] was synthesised as described in the literature. Treatment of indene with 3 equivalents of bromine in refluxing carbon tetrachloride, while being irradiated with a 150 W projector lamp gave the title compound **11** in 91% yield. We assume that indene undergoes first a bromine addition reaction. Further bromination of the formed dibromide **2** gives the tribromide **11** with the *trans,trans*-configuration. The exact configuration of this tribromide **11** was proved by X-ray analysis.[10a] In order to rationalise the exclusive formation of **11**, we have carried out some AM1 calculations for the all possible isomers. AM1 calculations show that the *trans,trans*-isomer **11** has about 0.79 and 1.06 kcal mol^{-1} lower heat of formation than the *trans,cis*-**12** and *cis,cis*-isomer **13**, respectively (Table 2). The formed product **11** is the thermodynamically most stable one.



Scheme 1

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Table 1 NMR spectral data of some disubstituted indane derivatives

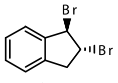
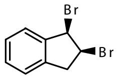
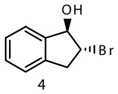
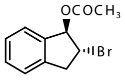
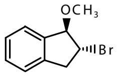
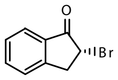
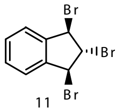
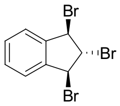
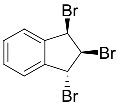
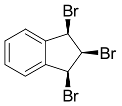
Compound	^{1}H NMR Resonances in ppm							
	H-1	H-2	H-3	H-3′	Subs.	Aromatic	Coupling constants *J*/Hz	^{13}C NMR
 2	br. s 5.5	dt 4.8	dd 3.7	br. d 3.2	—	m 7.3–7.5	J_{23} = 5.2 $J_{23'}$ = 1.2 $J_{33'}$ = 17.2	140.5, 140.4 129.6, 127.9 125.9, 125.3 57.6, 54.3 41.4.
 3	d 5.4	ddd 4.31	dd 3.19	dd 3.12	—	m 7.3–7.5	J_{12} = 5.0 J_{23} = 8.8 $J_{23'}$ = 6.5 $J_{33'}$ = 15.6	141.7, 140.5 129.4, 127.8 124.9, 124.3 58.5, 50.0 40.6.
 4	d 5.3	ddd 4.3	dd 3.8	dd 3.3	br. s 2.5	m 7.3	J_{12} = 5.4 J_{23} = 7.2 $J_{23'}$ = 7.5 $J_{33'}$ = 16.2	141.6, 139.7 129.0, 127.6 124.5, 124.1 83.4, 54.5 40.4
 5	d 6.18	m 4.37–4.33	dd 3.56	dd 3.14	s 1.97	m 7.32–7.11	J_{12} = 3.6 J_{23} = 6.8 $J_{23'}$ = 4.0 $J_{33'}$ = 16.8	
 7	d 4.83	ddd 4.35	dd 3.56	dd 3.1	s 3.48	m 7.1–7.3	J_{12} = 3.6 J_{23} = 6.8 $J_{23'}$ = 4.8 $J_{33'}$ = 16.8	
 8	—	dd 4.53	dd 3.7	dd 3.34		d, 7.74 dt, 7.57 m, 7.49–7.33	J_{23} = 7.5 $J_{23'}$ = 3.1 $J_{33'}$ = 18.1 J_{67} = 7.5 J_{56} = 7.5 $J_{46'}$ = 1.1	
 11	d 5.61	t 5.00	d 5.61	dd 3.1	s 3.48	AA′BB′ 7.49–7.43	J_{12} = 2.0 J_{23} = 2.0	140.3, 130.6 126.1, 57.7 52.6.

Table 2 AM1 optimised relative energies of the tribromides **11, 12** and **13**

Relative energies	 **11**	 **12**	 **13**
kcal/mol	0.00	0.79	1.06

For further functionalisation of the indane skeleton, the tribromide **11** was reacted with silver acetate in ether to give the bromodiacetate **14** in 86% yield. The symmetrical *trans,trans*-configuration was easily determined from the NMR spectra. This result clearly indicates that replacement of two bromine atoms yields *trans,trans*-bromodiacetoxyindane by way of a cyclopentenebromonium ion. The expected stereoselectivity was not observed by the treatment of **11** with silver sulfate in methanol and with silver nitrate in ether. In the first case, the isomeric bromodimethoxyindanes **15** and **16** were formed in a ratio of 3:1 where, contrary to the silver acetate reaction, the *trans,cis*-isomer **15** was formed as the major product.

Reaction of the tribromide **11** with silver nitrate in ether resulted in the formation of a isomeric mixture consisting of **17** and **18** where the *trans,cis*-isomer **17** was formed as the major product in a ratio of 2:1 (total yield 88%).

In summary, a short and simple method for the preparation of various di- and trisubstituted indane derivatives has been accomplished starting from dibromo- and tribromoindane **2** and **11**.

Experimental

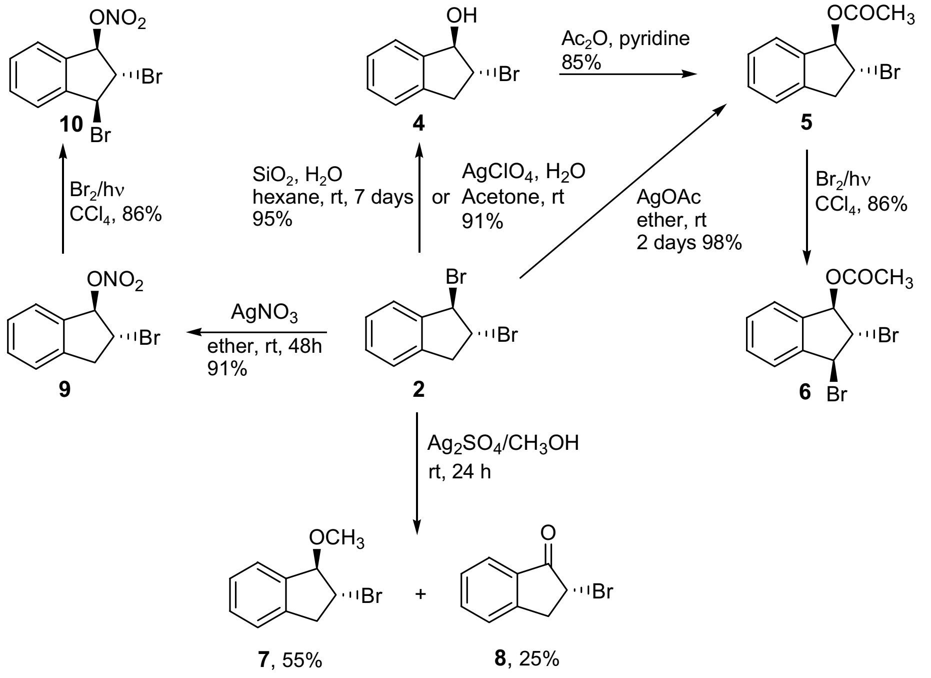
General: Melting points were determined on a Büchi model 530 apparatus and are uncorrected. IR spectra were recorded on a Mattson model 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on 400 (100) MHz spectrometers (400 MHz Bruker). Mass spectra (electron impact) were recorded at 70 eV (VGZabSpec range 1000 EI). Column chromatography was performed on silica gel (60–200 mesh) from the Merck Company. TLC was carried out on Merck 0.2 mm silica gel 60 F254 analytical aluminum plates.

Electrophilic addition of bromine to indene (**1**): To a solution of bromine (1.33 g, 8.3 mmol) in CCl_4 (1 ml) in a 10 ml of round-bottom flask, 0.964 g (8.3 mmol) of indene (**1**) (without solvent) was added by Pasteur pipette carefully at room temperature and two phases were formed. The reaction flask was shaken intensively for 5 min to give a red oily residue (2.08 g; 91%). The ^{1}H NMR analysis of the reaction mixture indicated the formation of **2** and **3** in a ratio of 2:1.

Synthesis of trans-1,2-dibromoindane (**2**): To a magnetically stirred solution of indene (0.96 g, 8.3 mmol) in CH_2Cl_2 (15 ml) cooled to 0°C (ice bath) was added dropwise a solution of bromine (3.96 g, 24.8 mmol) in CH_2Cl_2 (5 ml) during 30 min. After completion of the addition, the unreacted bromine and solvent were removed *in vacuo* at 20°C immediately. The red oily residue was filtered through a short basic alumina (15 g) eluting with *n*-hexane to give 2.20 g (96%) of colourless crystalline *trans*-dibromoindane (**2**) as the sole product. This product was crystallised from hexane by standing in a refrigerator overnight (m.p. 30–31°C, Lit. m.p. 29–31°C,[7c] 30–33°C[7b]).

cis-1,2-Dibromoindane (**3**): Spectroscopic data were extracted from a mixture consisting of *cis*- and *trans*-dibromides (Table 1).

Bromine-catalysed configuration isomerisation of cis-dibromide (**3**) *to trans-dibromide* (**2**): To a magnetically stirred mixture of *trans*- and *cis*-dibromide **2** and **3** (0.314 g, 1.14 mmol, in a ratio of 2:1) in 5 ml CCl_4, a solution of bromine (175 mg, 1.1 mmol) in CCl_4 (0.5 ml) was added at room temperature. The reaction mixture was

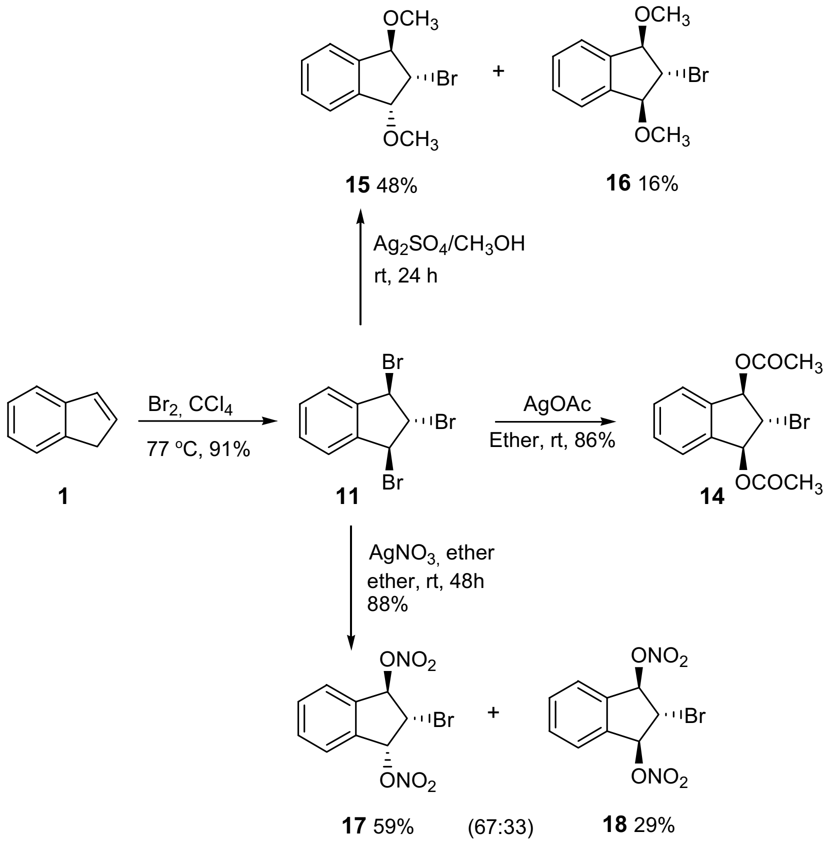


Scheme 2

stirred at room temperature for 1 h. After removal of the solvent at reduced pressure, the ^{1}H NMR analysis of the residue indicated the quantitative conversion of *cis*-dibromide **3** into *trans*-dibromide **2**.

Silver ion-promoted hydrolysis of trans-*dibromoindane* **2:** To a magnetically stirred solution of **2** (0.46 g, 1.70 mmol) in acetone (10 ml) was added a solution of $AgClO_4$ (0.70 g, 3.40 mmol) in aqueous acetone (10 ml acetone/5 ml H_2O) at room temperature over 5 min. The resulting mixture was stirred at room temperature for 30 min. The precipitated AgBr was removed by filtration. To the filtrate was added methylene chloride (50 ml) and the organic layer was washed with water (2 × 30 ml) and dried over Na_2SO_4. After removal of the solvent, the residue was crystallised from methylene chloride–hexane (3:1, 20 ml) by standing in refrigerator to give **4**, colourless needless, (0.33 g, 91%). M.p. 128°C. Lit. m.p. 129.5–130°C,[7b] 126–127°C,[9e] 129–130.5°C[9b]).

Silica gel promoted hydrolysis of trans-*dibromoindane* **2:** A mixture of *trans*-dibromoindane **2** (1.45 g), aqueous silica gel (10 g silica gel/5 g H_2O) and *n*-hexane (50 ml) was magnetically



Scheme 2

stirred at room temperature over a week. Reaction progress was monitored by TLC. After completion of the reaction, silica gel was filtered off and washed with CH_2Cl_2 (100 ml). After removal of the solvent from the combined solutions, the residue was crystallised from methylene chloride–hexane by standing in refrigerator to give **4** (95%).

Reaction of trans-dibromide **2** *with silver acetate*: A mixture of silver acetate (0.66 g, 4.00 mmol), dibromoindane **2** (1.00 g, 3.6 mmol) and molecular sieves (3Å, 0.50 g) in freshly distilled dry ether (50 ml) was stirred magnetically at room temperature for two days. Reaction progress was monitored by TLC. The precipitated silver bromide was removed by filtration. After removal of the solvent, the residue was crystallised from methylene chloride–hexane (1/3; 10 ml) to give *trans-2-bromo-2,3-dihydro-1H-inden-1-yl acetate* **5**, colourless needles, (0.88 g, 98%). M.p. 54–55°C.

Reaction of bromohydrin **4** *with acetic anhydride:* To a cooled solution of 2 g of bromohydrin **4** in 15 ml pyridine was added dropwise 2 ml of acetic anhydride with stirring. The reaction mixture was stirred at room temperature overnight, and water added (100 ml). The organic layer was separated and washed with cold 10% HCl, water and dried (K_2CO_3). After evaporation of the solvent, the dark-coloured material was filtered through a short column (20 g alumina) eluting with hexane. The solvent was evaporated. The residue was crystallised from hexane–methylene chloride to give **5** (2.0 g, 85%).

Synthesis of trans,trans-1-acetoxy-2,3-dibromo-1,2,3-trihydro-1H-indene (**6**): To a magnetically stirred solution of **5** (2.41 g, 9.15 mmol) in CCl_4 (20 ml) in a photochemical reaction apparatus (60 ml) was added a solution of bromine (1.65 g, 10.3 mmol) in CCl_4 (15 ml) dropwise over 60 min while being irradiated with a 150 W projector lamp. The resulting reaction mixture was irradiated for additional 2 h at room temperature. The solvent was evaporated and the red oily residue was filtered through a short Al_2O_3 (15 g) column eluting with *n*-hexane. After removal of the solvent, the crystalline residue was recrystallised from hexane (10 ml) at room temperature to give 2,3-dibromoindanyl acetate **6** as colourless crystals (3.03 g, 86%). M.p. 56–57°C. Anal. Calcd for $C_{11}H_{10}Br_2O_2$: C, 39.6; H, 3.2. Found: C, 39.4; H, 2.8. ν_{max} (KBr) 3084, 2979, 2902, 1693, 1333, 1250, 1103, 762, 702, 644, 542 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.2–7.4 (m, 4H, aryl), 6.2 (d, J_{12} = 2.7 Hz, 1H, H-1), 5.3 (d, J_{23} = 3.0 Hz, 1H, H-3), 4.5 (t, J = 2.8, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 142.0, 138.4 131.0, 130.4, 126.5, 126.4, 82.1, 55.7, 53.1, 21.3.

Silver ion promoted hydrolysis of trans-dibromindane **2** *in methanol*: A mixture of silver sulfate (1.50 g, 4.8 mmol), dibromoindane **2** (1.32 g, 4.8 mmol) and molecular sieve (3Å, 0.50 g) in dry and freshly distilled methanol (50 ml) was stirred magnetically at room temperature for 1 day. The precipitated silver bromide was removed by filtration. After removal of the solvent, the residue was chromatographed on silica gel (100 g) eluting with hexane/ethyl acetate in ratio of 9 : 1. The first fraction gave 2-bromo-1-methoxyindane **7**,[7d,9b] 0.68 g, 55%. The second fraction was identified as *2-bromoindanone* (**8**)[9] (0.29 g, 25%).

Synthesis of trans-2-bromoindanyl nitrate (**9**): A mixture of silver nitrate (0.55 g, 3.3 mmol), dibromoindane **2** (0.6 g, 2.2 mmol) and molecular sieve (3Å, 0.50 g) in dry and freshly distilled ether (50 ml) was stirred magnetically at room temperature for two days. The precipitated silver bromide was removed by filtration. After removal of the solvent, the crystalline residue was crystallised from ether–hexane (1/3; 10 ml) to give 2-bromoindanyl nitrate **9**, colourless crystals, m.p. 73–74°C (0.51 g, 91%). Anal. Calcd for $C_9H_8BrNO_3$: C, 41.9; H, 3.1; N, 5.4. Found: C, 41.75; H, 3.0; N, 5.3. ν_{max} (KBr) 3090, 1630, 1460, 1280, 1252, 836, 764, 580 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.5–7.3 (m, 4H, aryl), 6.4 (d, J_{12} = 1.7 Hz, 1H, H-1), 4.6 (ddd, J = 6.1, 1.9 and 1.7 Hz, 1H, H-2), 3.8 (dd, A-part of AB system, J = 17.6 and 6.1 Hz, 1H, H-3), 3.3 (dd, B-part of AB system, J = 17.6 and 1.9 Hz, 1H, H-3'). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 133.8, 131.1, 127.9, 126.9, 125.4, 92.4, 47.6, 41.6; Ms, *m/z* 257/259 (M^+, 3), 211/213 (M^+-NO_2, 8), 195/197 (M^+-NO_2, 100), 131 (15).

Synthesis of trans, trans-2,3-dibromo-1,2,3-trihydro-1H-indenyl nitrate (**10**): To a magnetically stirred solution of **9** (0.46 g, 1.92 mmol) in CCl_4 (20 ml) in a photochemical reaction apparatus was added dropwise a solution of bromine (0.41 g, 2.56 mmol) in carbon tetrachloride (15 ml) over 30 min while the reaction flask was irradiated by 150 W projector lamp. After additional irradiation for 2 h at room temperature, the solvent was evaporated. The yellow oily residue was filtered through a short Al_2O_3 (15 g) column eluting with *n*-hexane. After removal of the solvent, the solid residue was crystallised from ether–hexane by standing in refrigerator overnight to give **10** (0.51 g, 86%). M.p. 59–60°C, colourless crystals; Anal. Calcd for $C_9H_7Br_2NO_3$: C, 32.1; H, 2.1; N, 4.2. Found: C, 32.0; H, 2.0; N, 4.1. ν_{max} (KBr) 3031, 3007, 2901, 1629, 1460, 1286, 1271, 837, 751, 705, 678, 630, 583. cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.36 (m, 4H, aryl), 6.33 (d, J_{23} = 1.1 Hz, 1H, H-3), 5.40 (d, J_{12} = 1.4 Hz, 1H, H-1), 4.71 (dd, J = 1,4 and 1.1 Hz, 1H, H-2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 133.8, 132.0, 130.5, 127.1, 126.5, 90.0, 52.9, 51.34. Ms *m/z* (CI, NH_3) 353/355/357 ($M^+ + NH_3$,).

Trans,trans-1,2,3-tribromo-1,2,3-trihydro-1H-indene (**11**): was synthesised as described in the literature.[10] Colourless crystals from chloroform, m.p.133–134°C (Lit.[7a] m.p. 134.5–135°C) were obtained in a yield of 91% (1.95 g).

Trans,trans-1,3-diacetoxy-2-bromo-1,2,3-trihydro-1H-indene (**14**): A mixture of silver acetate (1.76 g, 10.5 mmol), tribromoindane **11** (1.50 g, 4.22 mmol) and molecular sieve (3 Å, 0.50 g) in dry and freshly distilled ether (50 ml) was stirred magnetically at room temperature for two days. The precipitated silver bromide was removed by filtration. After removal of the solvent, the crystalline residue was crystallised from methylene chloride–hexane (1/3; 10 ml) to give 1,3-diacetoxy-2-bromoindane **14**. Colourless crystals (1.14 g, 86%), m.p. 141–142°C. Anal. Calcd for $C_{13}H_{13}BrO_4$: C, 49.9; H, 4.2. Found: C, 50.2; H, 4.3. ν_{max} (KBr) 2989, 2360, 1734, 1375, 1227, 1201, 1120, 1030, 760, 746, 615, 451 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, AA'BB' system, 4H, aryl), 6.18 (d, J_{12} = J_{23} = 4.6 Hz, 2H, H-1 and H-3), 4.22 (t, J_{12} = J_{23} = 4.6 Hz, 1H, H-2), 2.1 (s, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 139.4, 130.4, 125.8, 81.0, 52.4, 21.2.

Silver ion promoted hydrolysis of trans,trans-tribromoindane **11** *in methanol*: A mixture of silver sulfate (0.93 g, 2.99 mmol), tribromoindane **11** (1.32 g, 4.8 mmol) and molecular sieves (3 Å, 0.50 g) in dry and freshly distilled methanol (30 ml) was stirred magnetically at room temperature for 1 day. The precipitated silver bromide was removed by filtration. After removal of the solvent, the oily residue was chromatographed on silica gel (120 g) with hexane/ethyl acetate (9:1).

The first fraction consisted of the *trans-cis-2-bromo1,3-dimethoxyindane* **15**: Colourless oily liquid 0.46 g (48%). ν_{max} (liquid) (purity over 95%): 2927, 2824, 1462, 1348, 1273, 1214, 1121, 1085, 762 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4H, aryl), 4.89 (d, J_{12} = 3.5 Hz, 1H, H-1), 4.73 (d, J_{23} = 4.7 Hz, 1H, H-3), 4.49 (dd, J_{23} = 4.7 and 3.5 Hz, 1H, H-2), 3.49 (s, 3H, OCH_3), δ 3.40 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 139.7, 129.1, 128.9, 125.5, 125.3, 88.7, 82.3, 58.1, 56.9, 56.1.

As the second fraction, *trans-trans-2-bromo-1,3-dimethoxyindane* **16** was isolated. 0.15 g (16%), colourless crystals from ether–hexane, m.p. 143–144°C. ν_{max} (KBr): 2927, 2824, 1460, 1353, 1290, 1263, 1112, 1081, 722 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, AA'BB' system, 4H, aryl), 5.04 (t, J_{12} = J_{23} = 4.4 Hz, 1H, H-2) 4.48 (d, J_{12} = J_{23} = 4.4 Hz, 2H, H-1 and H-3), 3.49 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 128.7, 124.4, 81.5, 60.10, 57.2. ppm.

Synthesis of cis,trans- and trans,trans-2-bromo-1,2,3-trihydro-1H-indenyl-1,3-dinitrate (**17–18**): A mixture of silver nitrate (1.78 g, 10.5 mmol), tribromoindane **11** (1.50 g, 4.22 mmol) and molecular sieves (3 Å, 0.50 g) in dry and freshly distilled ether (50 ml) was stirred magnetically at room temperature for two days. The precipitated silver bromide was removed by filtration. After removal of the solvent, the colourless oily residue (1.09 g, 88%) was analysed by ^1H NMR spectroscopy which showed the presence of a mixture consisting of the *cis,trans-* **17** and *trans,trans-* isomer **18**. Attempts to separate these isomers failed. The relative percentage of products **17** and **18** was determined from the integration of ^1H NMR signals and found to be in a ratio of 67:33.

Cis-trans-dinitrate **17**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 4H, aryl), 6.42 (d, J_{12} = 2.6 Hz, 1H, H-1), 6.30 (d, J_{23} = 5.0 Hz, 1H, H-3), 4.83 (dd, J = 5.0 and 2.6 Hz, 1H, H-2). ^{13}H NMR (400 MHz, $CDCl_3$) δ 136.2, 134.1, 131.7, 131.2, 126.8, 125.9, 88.7, 82.0, 50.3.

Trans,trans-dinitrate **18:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (br s, 4H, aryl), 6.24 (d, J_{12} = J_{23} = 1.0 Hz, 2H, H-1 and H-3), 4.4 (t, J_{12} = J_{23} = 1.0 1H, H22). ^{13}C NMR (100 MHz, $CDCl_3$) δ, 135.7, 132.0, 127.3, 89.2, 47.8.

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