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Towards the *cis*-Bromination of Double Bonds

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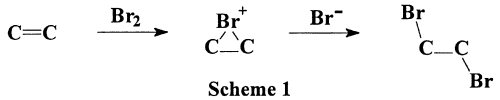
Simple bromination of olefins almost invariably yields the *trans*-1,2-dibromo-product, and in many cases the corresponding *cis*-product is an unknown compound. Approaches towards a reagent which will generally, mildly and stereospecifically *cis*-brominate olefins are now discussed.

Manuscript received: 1 March 2001.

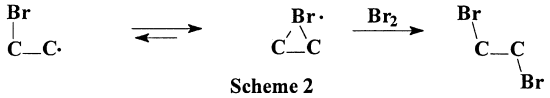
Introduction

Electrophilic bromination of simple olefins almost invariably[1–4] yields *trans*-1,2-dibromides. The reaction normally proceeds through a bridged bromonium ion which is then attacked by bromide from the rear (Scheme 1). When the olefin is within a cyclohexyl system, the major product from this route is normally the *trans-diaxial*-dibromide. Some exceptions leading to *cis*-1,2-dibromides are known, but these examples involve 'complicated' olefins, either with delocalized double bonds, or with serious hindrance at one face, or with geometry such that other incorporated functional groups can participate during the olefinic bromination.



Scheme 1

Radical addition of bromine to olefins, when it can be made to occur,[5] is normally also a *trans* process, again, with evidence[6,7] for bridging in the radical intermediate (Scheme 2). Radical bromination of monobromo compounds may also lead to 1,2-dibromo products, but again (Scheme 2), the observed product is normally[6,8] *trans*-disubstituted.



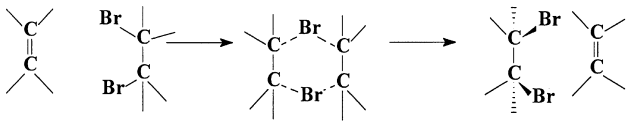
Scheme 2

For these reasons, *cis*-1,2-dibromo compounds are not well known, and *cis*-dibromides derived from many readily-available olefins have not been described. If a reagent were available to readily *cis*-brominate olefins it would therefore make immediately available a large number of novel compounds. Furthermore, the *cis*-bromination of di- or tri-substituted cyclic olefins will normally provide compounds with a bromine and a hydrogen vicinal and antiperiplanar, allowing dehydrobromination to then afford a range of generally-novel vinyl bromides.

We now discuss attempts to find a reagent which will mildly and generally *cis*-brominate olefinic double bonds. While we have not yet succeeded in this aim, we describe preliminary approaches, together with a number of novel compounds.

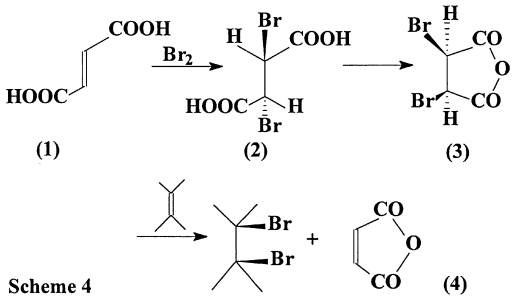
Discussion and Results

The discussion above indicates that a suitable *cis*-brominating reagent cannot involve Br^+ or $Br^\bullet$. We have therefore explored reagents which might deliver two bromine atoms to the same side of the olefin through a cyclic six-membered transition state (Scheme 3).



Scheme 3

There are two problems with Scheme 3, as drawn. Firstly, it is degenerate as written and requires adjustment to drive it to the right-hand side. Secondly, the starting agent is a *cis*-dibromide; the very material we argue is in short supply. We sought to overcome both these problems by employing the *cis*-dibromosuccinic anhydride (3) (Scheme 4). This compound was expected to be available by normal *trans*-

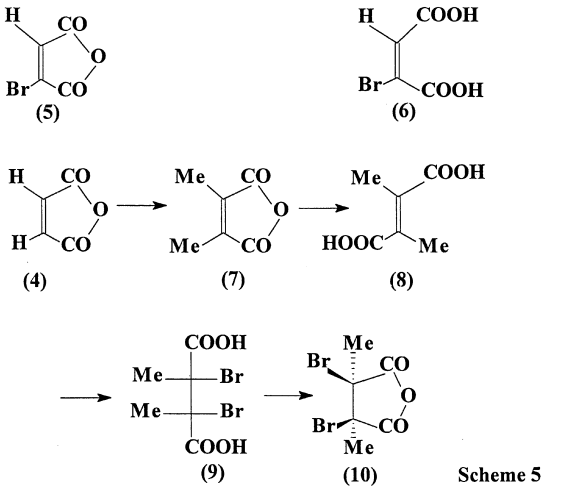


Scheme 4

 10.1071/CH01016 0004-9425/01/020117

dibromination of fumaric acid (1), followed by cyclization to the succinic anhydride (3). The structure (3) was then expected to provide a driving force through the cyclic transition state, since it leads to the conjugated maleic anhydride (4) as product. As an added bonus, we anticipated that anhydride (4) would then be easily removed from the brominated product in work-up.

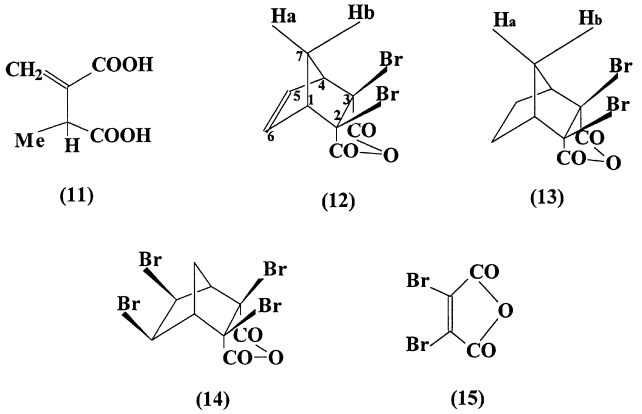
Attempts to convert the *meso*-dibasic acid (2) into the required, but unknown, anhydride (3) failed by the literature methods[9–13] for anhydride formation. The primary product was the unsaturated anhydride (5), sometimes formed together with the corresponding diacid (6). The required product (3) is apparently thermally unstable, readily eliminating hydrogen bromide to alleviate the steric strain associated with two *cis-vicinal* bromine atoms.



Scheme 5

To overcome this problem we have examined compounds structured without an α-hydrogen. The *meso*-dibasic acid (9) (Scheme 5) is described in the literature,[14] although it is not available by simple bromination of the olefin (8) and data reported for the compound are inconclusive. However, vapour-phase bromination of solid compound (8) over 14 days afforded the dibromide (9) which could then be converted to the thermally stable novel anhydride (10). Attempts using compound (10) as a *cis*-brominating agent are discussed below.

During the synthetic steps of Scheme 5 it is necessary to isomerize about the double bond going from (7) to (8). This can be achieved by the high temperature alkaline treatment of compound (7), in which the *cis*-dicarboxylate dianion rearranges to the more stable *trans*-dianion. However, in our hands, as in others,[15–17] this step is accompanied by the formation of considerable amounts of the undesired methylitaconic acid (11). While this compound can be removed from the mixture through anhydride formation (when compound (8) does not react), its undesired formation encouraged us to explore further into compounds in which double bond migration could not occur. Thus, we have examined the bicyclic anhydrides (12)–(14). These compounds are substituted succinic anhydrides, with the C2 and C3 bromines *cis*, but with no hydrogens at C2 or C3 to enable dehydrohalogenation, and with little likelihood of



elimination or double bond migration into the adjacent bridgehead carbons (C1 and C4) due to Bredt strain.

Compound (12) was first reported[18] by Diels and Alder, and is available from the cycloaddition reaction between cyclopentadiene and dibromomaleic anhydride (15). The *endo* configuration has been demonstrated[18,19] by using the standard method of bromolactonization, and this stereochemistry is now confirmed by an X-ray crystallographic analysis (Fig. 1). This structure provides the expected torsion of ca. 0° between the two bromine atoms.

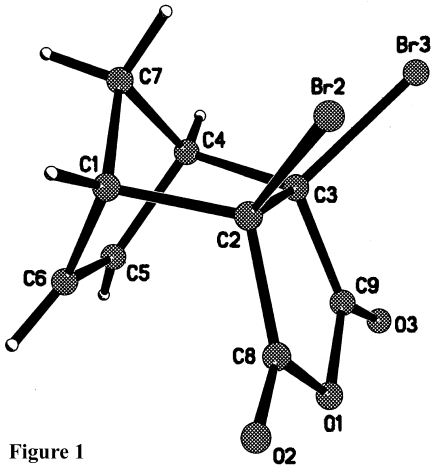


Figure 1

Compound (12) is a stable compound but, with an available double bond to undergo further bromination, cannot in its own right be a satisfactory brominating agent. Hydrogenation afforded compound (13), potentially more useful, while bromination afforded the novel tetrabromide (14). The X-ray structure of compound (14), provided in Figure 2, shows the *syn-exo* disposition (see below) of the C5 and C6 bromines.

Compound (14) is stable to recrystallization from benzene, but it decomposes quantitatively in more polar solvents such as acetone to afford the novel dibromide (16a). When this reaction was followed by NMR spectroscopy, transient signals for a second, very similar, product could be seen. This latter compound, which could not be isolated, is presumed to be the anhydride (17). We have been unable to find conditions to convert diacid (16a) into the anhydride

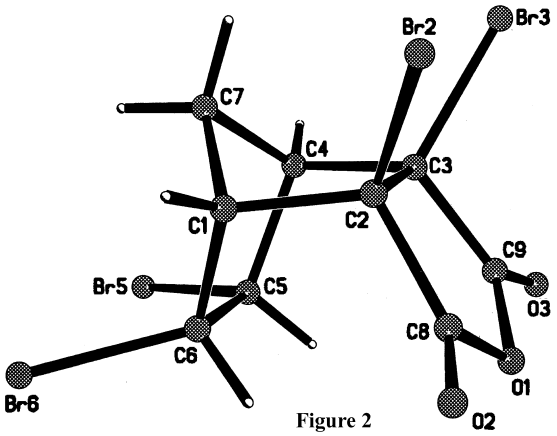
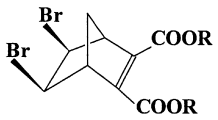
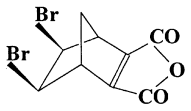


Figure 2



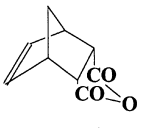
(16) a R=H
b R=Me



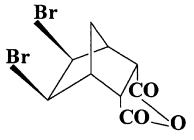
(17)

(17), and note that other workers[20,21] also report difficulties in achieving anhydride formation by ring closure of similar compounds.

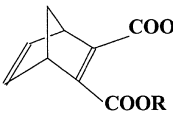
Compound (16a) was readily converted into the diester (16b) which provided appropriate spectral data. For comparison and complete identification purposes, the same product (16b) was synthesized by an independent and ostensibly simple route.



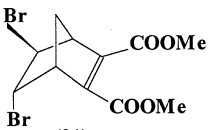
(18)



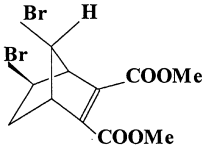
(19)



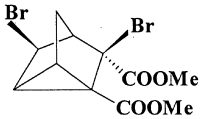
(20) a R=H
b R=Me



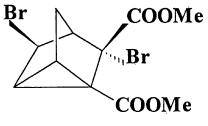
(21)



(22)



(23)



(24)

It has been claimed[22–25] that the addition of bromine in non-polar solvents, to the C5–C6 double bond of compounds such as (18) occurs predominantly *syn* and *exo*, due to steric and/or electronic blocking by the *endo*-anhydride moiety. We now confirm by X-ray crystallographic analysis that the major bromination product from compound (18) is dibromide (19) (Fig. 3). On the other hand, at least five major products (all present in the same TLC spot!) were obtained when diene diester (20b) was brominated under similar conditions. These products were identified as compounds (16b) (10%), (21) (10%), (22) (46%), (23) (13%), and (24) (20%). Compound (16b) was identical with the material described above. The structures of the other rearranged compounds are discussed below.

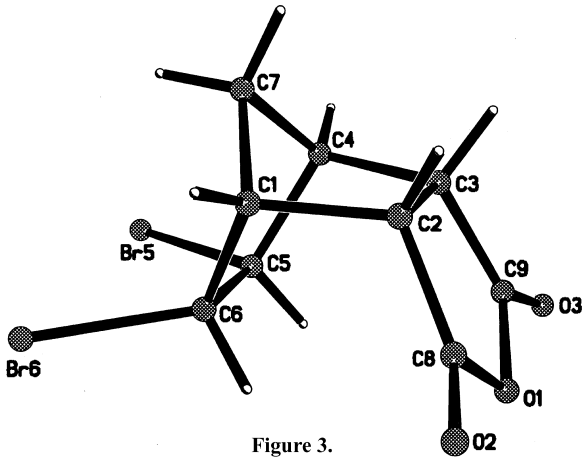


Figure 3.

Table 1. ^{13}C NMR shifts (δ) in (D_6)acetone solution

Compound	C1,4	C2,3	C5,6	C7	C8,9
(12)	58.4	66.1	138.2	51.9	167.0
(13)	54.3	69.3	25.6	39.9	167.4
(14)	49.7	65.6	63.7	36.6	166.1
(16a)	51.5	147.4	57.5	43.1	165.3
(16b)[A]	52.5	143.8	55.8	43.8	163.6
(19)	52.0	49.9	53.0	38.4	171.6
(25)	54.4	48.2	52.4	30.4	171.8

[A] With 50.6, OMe; data in $CDCl_3$.

Table 2. ^{1}H NMR shifts (δ) in (D_6)acetone solution

Compound	H1,4	H2,3	H5,6$_{exo}$	H7a	H7b
(12)	3.68	–	6.51[A]	2.37	2.57
(13)[B]	3.09	–	1.95	2.03	2.47
(14)	3.43	–	4.64	2.83	2.72
(16a)	3.66	–	4.56	2.36	2.18
(16b)[C]	3.48	–	4.23	2.40	2.05
(19)	3.13	3.85	4.52	2.47	2.05
(25)	2.98	3.44	4.66	2.26	1.48

[A] Vinyl protons.
[B] With 1.44, H5,6$_{endo}$.
[C] With 3.78, s, two OMe.

NMR spectral data for the symmetrical bromides (12), (13), (14), (16a,b), and (19) are collected in Tables 1–3, with structure (25) also included for comparison. The chemical shift data is unexceptional. The relative chemical shifts of the H5, H6 *exo*- and *endo*-protons in compound (13) were in accord with similar compounds, with the *exo* occurring at lower field (δ 1.95) than the *endo* system (δ 1.44). The proton coupling constants (Table 3) provided uniform results. The bridging methylene protons H7a and H7b

Table 3. ^{1}H NMR coupling constants (Hz)

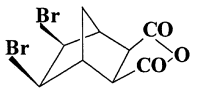
Compound	$J_{1,7a(4,7a)}$	$J_{1,7b(4,7b)}$	$J_{1,5(4,6)}$	$J_{1,6(4,5)}$	$J_{7a,7b}$	$J_{5,7a(6,7a)}$	$J_{5,7b(6,7b)}$
(12)	1.6	1.8	0.4	2.5	–10.1	0	2.0
(13)[A]	1.5	1.5	—	1.5, 3.5	–11.0	0	2.8
(14)	1.5	1.5	0	0	–12.3	0	2.3
(16a)	1.6	1.9	0	0	–10.0	0	1.9
(16b)	1.4	1.8	0	0	–11.1	0	2.1
(19)[B]	1.5	1.5	0	0	–10.7	0	2.2
(25)[C]	1.5	1.5	0	0.2	–12.3	0	2.1

[A] With $J_{5exo,5endo}$ ($J_{6exo,6endo}$) = 10 Hz.
[B] With $J_{1,2}$ ($J_{3,4}$) = 3.6; and $J_{1,3}$ ($J_{2,4}$) = 2.2 Hz.
[C] With $J_{1,2}$ ($J_{3,4}$) = 0.2; and $J_{2,7a}$ ($J_{3,7a}$) = 1.5 Hz.

Table 4. Bond lengths for compounds (12), (14) and (19)

Atoms	Distance (Å)		
	Compound (12)	Compound (14)	Compound (19)
C(1)–C(2)	1.570(10)	1.550(12)	1.554(7)
C(1)–C(6)	1.516(10)	1.518(11)	1.531(7)
C(1)–C(7)	1.549(10)	1.549(12)	1.533(7)
C(2)–C(3)	1.581(10)	1.528(12)	1.528(7)
C(2)–C(8)	1.518(10)	1.553(12)	1.484(8)
C(2)–Br(2)	1.957(7)	1.939(8)	—
C(3)–C(4)	1.570(10)	1.579(12)	1.561(7)
C(3)–C(9)	1.535(11)	1.511(12)	1.501(8)
C(3)–Br(3)	1.954(7)	1.933(8)	—
C(4)–C(5)	1.542(10)	1.559(11)	1.534(6)
C(4)–C(7)	1.542(10)	1.526(11)	1.545(7)
C(5)–C(6)	1.311(11)	1.535(11)	1.551(7)
C(5)–Br(5)	—	1.936(8)	1.953(5)
C(6)–Br(6)	—	1.937(8)	1.955(5)
C(8)–O(1)	1.409(9)	1.395(11)	1.406(7)
C(8)–O(2)	1.202(9)	1.172(10)	1.187(6)
C(9)–O(1)	1.397(9)	1.394(10)	1.400(6)
C(9)–O(3)	1.195(9)	1.174(10)	1.184(6)

coupled each other by $J \approx -11$ Hz. The signal for H7a normally provided a doublet of triplets, showing coupling to the bridgehead protons. The signal for H7b normally showed additional long-range W-coupling to the protons at H5 and H6, and therefore appeared as a complex multiplet. The signals for H5 and H6 appeared as a doublet in compounds (14), (16a,b), and (19), but were further complicated by additional coupling in compounds (12), (13), and (25). The *endo* C5, C6 protons in compounds (14), (16a,b), (19), and (25) make a torsion angle (H6–C6–C1–H1 = H5–C5–C4–H4) of about ±90°, providing a near zero coupling between neighbouring protons H1 and H6 (= H4 and H5). The signals for H1, H4 in compounds (14) and (16a,b) then appear as a triplet, coupled only to two H7. Compound (25) also shows only a similar, small coupling between H1 and H2 (= H4 and H3). H1 and H4 in compound (25) are then a broadened triplet, both H2 + H3 and H5 + H6 are broadened doublets, while H7a is a doublet of fine pentuplets and H7b is a doublet of fine triplets of triplets.



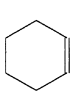
(25)

Table 5. Bond angles and selected torsion angles for compounds (12), (14) and (19)

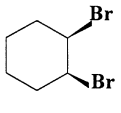
Atoms	Angle (degrees)		
	Compound (12)	Compound (14)	Compound (19)
C(1)–C(2)–C(3)	102.5(6)	104.5(7)	103.3(4)
C(1)–C(2)–C(8)	113.2(6)	113.9(7)	116.1(4)
C(1)–C(2)–Br(2)	111.8(5)	109.3(5)	—
C(1)–C(6)–C(5)	108.1(7)	103.8(6)	104.2(4)
C(1)–C(6)–Br(6)	—	110.6(6)	110.8(4)
C(1)–C(7)–C(4)	93.9(6)	94.9(7)	94.6(4)
C(2)–C(1)–C(6)	106.4(6)	109.9(7)	108.4(4)
C(2)–C(1)–C(7)	99.5(5)	99.6(7)	100.3(4)
C(2)–C(3)–C(4)	102.4(5)	102.7(6)	104.0(4)
C(2)–C(3)–C(9)	103.7(6)	105.9(7)	105.7(5)
C(2)–C(3)–Br(3)	117.6(5)	118.1(6)	—
C(2)–C(8)–O(1)	110.1(6)	108.3(7)	109.7(5)
C(2)–C(8)–O(2)	129.8(7)	130.0(8)	132.0(6)
C(3)–C(2)–C(8)	104.4(6)	104.0(7)	104.8(5)
C(3)–C(2)–Br(2)	117.3(5)	118.6(6)	—
C(3)–C(4)–C(5)	106.0(6)	108.3(7)	109.8(4)
C(3)–C(4)–C(7)	99.6(6)	100.7(6)	99.9(4)
C(3)–C(9)–O(1)	110.2(6)	109.1(7)	108.5(5)
C(3)–C(9)–O(3)	129.6(7)	129.6(8)	131.8(6)
C(4)–C(3)–C(9)	113.5(6)	114.0(7)	115.2(5)
C(4)–C(3)–Br(3)	111.5(5)	109.0(5)	—
C(4)–C(5)–C(6)	107.9(7)	102.1(6)	102.5(4)
C(4)–C(5)–Br(5)	—	107.7(6)	108.6(4)
C(5)–C(4)–C(7)	100.2(6)	101.8(7)	101.2(4)
C(5)–C(6)–Br(6)	—	116.3(6)	116.9(3)
C(6)–C(1)–C(7)	100.9(6)	101.9(6)	101.9(4)
C(6)–C(5)–Br(5)	—	117.2(6)	116.3(3)
C(8)–C(2)–Br(2)	107.5(5)	106.6(6)	—
C(8)–O(1)–C(9)	111.6(6)	112.6(7)	111.1(6)
C(9)–C(3)–Br(3)	108.1(5)	107.5(5)	—
O(1)–C(8)–O(2)	120.0(7)	121.7(8)	118.3(6)
O(1)–C(9)–O(3)	120.2(7)	121.3(8)	119.7(6)
Br(2)–C(2)–C(3)–Br(3)	–0.4(7)	–0.3(9)	—
Br(5)–C(5)–C(6)–Br(6)	—	4.2(8)	7.7(5)

Crystallographic bond lengths for compounds (12), (14), and (19) are listed in Table 4, with bond angles in Table 5; where a comparison of data between the three compounds shows considerable consistency in both bond length and bond angle.

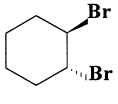
A preliminary survey to examine the usefulness of compounds (10), (13), and (14) as *cis*-brominating agents has not yet led to success. Cyclohexene (26) was chosen as a substrate since both *cis*- and *trans*-1,2-dibromocyclohexane, (27) and (28), respectively, are detectable and separable by gas chromatography (GC). This substrate, with one of the dibromides (10), (13) or (14), was heated in a wide range of solvents, both in the presence and absence of light. No evidence was detected for the formation of *cis*-1,2-dibromocyclohexane (27). Control tests with authentic



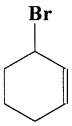
(26)



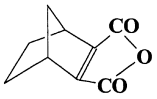
(27)



(28)



(29)



(30)

compound (27) showed that it was stable under our range of conditions. Starting anhydrides (10) and (13) remained essentially unchanged, although the fate of anhydride (14) was more difficult to ascertain since it was less stable to GC conditions. Extended and vigorous heating led to the formation of a number of products as observed by GC analysis. Some of these compounds were oxidation products derived from cyclohexene, as confirmed when neat cyclohexene alone was exposed to similar conditions. The only identifiable bromination products were the *trans*-isomer (28) (trace amounts) and the allylic bromide (29). The formation of compound (29) appeared to be independent of reaction conditions (solvent, dark/light) and its mode of formation is obscure but presumably involves the presence of radicals and/or free bromine. Traces of debromoanhydrides (7) and (30) could on occasion be observed from their respective dibromo starting materials (10) and (13).

The above results are disappointing in that they have failed to provide a reagent that will generally *cis*-brominate olefins. Additionally, these results suggest that further fine tuning of Scheme 3 would be unlikely to provide useful *cis*-dibromination results, and that a suitable reagent must therefore be sought in a different area.

The Compounds (21)–(24)

The compounds (21)–(24) were all separated from compound (16b) by extensive chromatography. All were colourless, viscous oils. Structural assignment was assisted by the work of McCulloch[26] who produced a range of analogous diiodo compounds by the iodination of compound (20b). Atomic connectivities were determined by using ^{1}H, ^{13}C (both ^{1}H coupled and decoupled), DEPT, ^{1}H–^{1}H-COSY and ^{1}H–^{13}C-HSQC NMR techniques.

Compounds (16b), (21), and (22) all provided a near-zero coupling between H4 and H5, indicating that the C5 bromine was *exo* in all these compounds. Compound (16b) shows a plane of symmetry in NMR studies, while the unsymmetrical (21) gave a 3.6 Hz coupling between H1 and H6, suggesting that the C6 bromine was *endo*, and showing that the two bromines in isomer (21) were *trans*.

Compound (22) provided a methylene group (C6) showing the expected vicinal couplings. The coupling between $H6_{endo}$ and H5 was large (8.1 Hz), suggesting a torsion angle of ca. 0°. Long-range couplings were observed from H7b to both H5 and $H6_{endo}$, and the bromine attached to C7 must therefore be *anti* to the ester groups as depicted in structure (22).

The tricyclic compounds (23) and (24) lacked the double bond present in the other compounds. A cyclopropyl ring was apparent in both these products from the large ^{1}H–^{13}C coupling (180 Hz)[27] between C1 and H1, and from the high-field chemical shifts for C1, C2 and C6. All evidence suggested that they were C3 epimers, and the chemical shifts of the two C7 protons were then used to distinguish them. Compound (23) provided H7a and H7b with similar chemical shifts (δ 2.40 and 2.57, respectively), consistent with both these hydrogens experiencing a similar *exo* bromine environment. In contrast, compound (24) provided H7a and H7b at different chemical shifts (δ 2.20 and 1.67, respectively), consistent with the more different environment around C7 in structure (24). A similar trend was noted[26] in the iodinated series.

Experimental

^{1}H and ^{13}C NMR spectra were recorded in (D_6)acetone solution unless otherwise indicated, upon a Jeol GX 400 spectrometer. ^{13}C multiplicities were assigned by the DEPT pulse sequence. GC analyses were most effectively performed upon a capillary column (5% phenylmethylpolysiloxane) with helium carrier gas and flame ionization detection in a Varian 3300 instrument, using Delta software. Preparative GC separations were achieved upon a Shimadzu GC9A instrument (OV101 column) with nitrogen carrier gas. Mass spectra were recorded upon a Hewlett Packard MSD 5970 spectrometer with a gas chromatographic inlet (5% phenylmethylpolysiloxane column), while HRMS data were obtained from a Kratos MS 25 RFA or a Finnigan 2001 spectrometer. Infrared data were measured in KBr discs for crystals, or as neat oils using a Perkin Elmer 1600 series FT-IR, unless otherwise stated. Column chromatography was performed over Kieselgel 60, 230–400 mesh. HPLC separations were run on Dynamax silica columns with refractive index detection, whereby new compounds were refined to > 99% (by NMR and GC) purity and analysed by microanalysis and/or HRMS.

X-Ray crystallographic data were collected from single-crystal samples mounted on a glass fibre. The diffractometer was a Siemens P4, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector using the program SMART (v5.045 Bruker AXS 1998) and a graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Processing used Siemens XSCANS data collection, Siemens SHELXTL data reduction, Siemens XSCANS cell refinement, SHELXS-97 direct method structure solution, and SHELXL-97 structure refinement by full-matrix least squares on F^2. Atomic coordinates, displacement parameters and observed and calculated structure factors have been deposited and are available upon request until 31 December 2006 from the *Australian Journal of Chemistry—an International Journal for Chemical Science*, P.O. Box 1139, Collingwood, Vic. 3066.

The meso*-Diacid (2)*

Fumaric acid (1) (20 g) suspended in water (150 mL) containing a few drops of phenophthalein indicator was stirred and titrated with sodium hydroxide solution (20% w/v) until the pink end-point. Potassium bromide (finely powdered, 81.9 g) was added portionwise until fully dissolved, followed by a solution of bromine (36.8 g) in aqueous potassium bromide (20% w/v, 100 mL) over 20 min. After 1 h, solid sodium bisulphite (3 g) was added, and the mixture acidified with hydrochloric acid (conc.). The product was filtered off and dried to give a white powder (32.2 g, 68%). *meso* (2*R*,3*S*)-2,3-Dibromosuccinic acid (2) gave irregular blocks from water, m.p. 276–278°C (lit.[28] 270–273°C). ^{1}H NMR δ 4.63, s. ^{13}C NMR δ 44.1, C2,3; 169.1, C1,4. IR 2920, 2675, 2543, 1699, 1463, 1423, 1296, 1181, 1146, 913, 778, 656, 583, 541 cm^{-1}.

Attempts to convert compound (2) into the unknown structure (3) by using acetyl chloride, acetic anhydride, dicyclohexylcarbodiimide, or thionyl chloride in pyridine all failed to produce the dibromoanhydride (3), but rather provided mixtures of compounds (5) and (6) which were identified by spectroscopic comparison with the literature.[29]

The Anhydride (7)

2,2′-Dimethylmaleic anhydride (7) was prepared from maleic anhydride (4) and 2-aminopyridine by the literature[30,31] method, to give pearly leaflets, > 99% pure by ^{1}H and ^{13}C NMR analysis, m.p. 92–93°C (lit.[30] 93–94°C). ^{1}H NMR δ 2.06, s. ^{13}C NMR δ 9.3, Me; 141.4, C 2,3; 167.2, C 1,4. IR consistent with the literature.[32] Mass spectrum: *m/z* 127 (M+1, 1%), 126 (M, 17), 82 (M–CO_2, 45), 54 (88), 53 (36), 51 (18), 50 (20), 39 (100).

The Diacid (8)

Anhydride (7) (5.0 g) dissolved in aqueous sodium hydroxide (3.2 g in 20 mL water) was heated to 185°C in a sealed bomb for 66 h. The solution was then cooled (ice) and acidified with six equal portions of hydrochloric acid (10.5 M, 7.6 mL total). After each addition of acid, the resultant precipitate was collected by filtration and the filtrates retained. The six precipitated fractions were identical (m.p. 92–94°C) and were combined to give unreacted anhydride (7) (1.52 g). Diacid (8) was then precipitated from the remaining filtrate by acidification with additional hydrochloric acid (10.5 M, 10.0 mL). The material was collected by filtration and dried to give the diacid (8) as a colourless powder (1.06 g). The material was pure by ^{1}H and ^{13}C NMR analysis and the corresponding dimethyl ester (diazomethane) gave a single gas-chromatographic peak. The mother liquors were then extracted with ether, and the extracts dried (Na_2SO_4). Evaporation afforded a fraction (1.4 g) which was comprised of a mixture of anhydride (7), diacid (8) and diacid (11) (ca. 1:5:6 by GCMS analysis of the corresponding dimethyl esters). This material (1.4 g) was then taken up in hot benzene, and the solvent decanted from the residual solids. This process was repeated several times and the solvent removed to afford anhydride (7) (0.23 g). The remaining residue was then recrystallized (water) and the diacid (8), which separated as needles, was removed by filtration. The resultant mother liquor was then evaporated to yield chiefly diacid (11), contaminated with small amounts of diacid (8).

(*E*)-2,3-Dimethylbut-2-enedioic acid (dimethylfumaric acid) (8) gave colourless needles, m.p. 236–238°C (water) (lit.[33] 241°C) (Found: C, 49.8; H, 5.6. Calc. for $C_6H_8O_4$: C, 50.0; H, 5.6%). ^{1}H NMR δ 2.07, s. ^{13}C NMR δ 17.6, two Me; 133.9, C 2,3; 170.3, C 1,4. IR 2989, 2878, 2678, 2567, 1700, 1411, 1378, 1317, 1289, 1200, 1100, 917, 872, 644, 561 cm^{-1}.

(*E*)-Dimethyl 2,3-dimethylbut-2-enedioate (dimethyl dimethylfumarate) had m.p. 39–40°C (lit.[17] 41–42°C). Mass spectrum: *m/z* 142 (6%), 141 (M–MeO, 41), 140 (M–MeOH, 100), 113 (35), 112 (26), 97 (7), 84 (17), 83 (24), 82 (14), 70 (9), 59 (56), 54 (30), 53 (46), 43 (55), 41 (50), 39 (35).

2-Methyl-3-methylenesuccinic acid (methylitaconic acid) (11) had ^{1}H NMR [abstracted from mixtures containing compounds (7), (8), and (11)] δ 1.36, d, Me; 3.60, dq, H2; 5.79, dd, H5; 6.31, d, $J_{Me,2}$ 7.2 Hz, $J_{2,5}$ 2.0 Hz, $J_{5,5}$ 2.0 Hz, H5′; consistent with the literature.[34,35] ^{13}C NMR δ 16.6, Me; 41.7, C2; 125.8, C5; 141.6, C3; 167.7, 175.1, C 1,4. Mass spectrum: *m/z* (as dimethyl ester) 172 (M, 3%), 157 (56), 141 (21), 140 (20), 113 (70), 81 (66), 59 (100), 53 (67), 41 (24), 39 (39).

Compound (11) was also identified and separated through its anhydride. The acid mixture (8) and (11) (0.21 g) was refluxed (2 h) with acetyl chloride (5 mL). The excess acetyl chloride was evaporated and the residue sublimed (0.03 mmHg, 70°C) to yield methylitaconic anhydride [the anhydride of structure (11)] (114 mg, 62%). This compound (2-methyl-3-methylenesuccinic anhydride) is a known compound,[36] m.p. 63°C (Found: C, 56.8; H, 4.9. $C_6H_8O_3$ requires C, 57.1; H, 4.8%). ^{1}H NMR δ 1.50, d, Me; 3.86, qt, H2; 5.96, m, H5; 6.41, m, $J_{Me,3}$ 7.5 Hz, $J_{3,5} \approx J_{3,5}$ 2.8 Hz, $J_{5,5}$ 2.8 Hz, H5′. ^{13}C NMR δ 15.0, Me; 40.0, C2; 124.7, C5; 138.6, C3; 165.6, 173.5, C 1,4. IR 1843, 1778, 1761, 1692, 1658, 1402, 1289, 1248, 1217, 1101, 1022, 964, 889, 814, 694, 612, 554 cm^{-1}. Mass spectrum: *m/z* 126 (M, 14%), 83 (2), 82 (M–CO_2, 39), 67 (4), 54 (83), 53 (40), 51 (21), 50 (24), 39 (100).

The Dibromide (9)

Diacid (8) (468 mg), in a pre-weighed beaker, was placed in a sealed dark-glass jar containing bromine (1–2 mL). The material was periodically weighed to determine bromine uptake, which appeared to be complete after 14 days. During this time, the material in the beaker was mixed daily, and the bromine replenished as required. Evaporation of the excess bromine afforded compound (9) as an orange solid (0.93 g, 94%), > 99% pure by ^{1}H and ^{13}C NMR analysis. The corresponding dimethyl ester (diazomethane) gave a single peak by GCMS analysis.

(2*R*,3*S*)-*2,3-Dibromo-2,3-dimethylsuccinic acid* (*meso*-2,3-dibromo-2,3-dimethylsuccinic acid) (9) gave colourless crystals (water), m.p. 203–204°C (Found: C, 23.6; H, 2.6. $C_6H_8Br_2O_4$ requires C, 23.7; H, 2.7%). ^{1}H NMR δ 2.23, s, Me. ^{13}C NMR δ 28.8, two Me; 65.7, C 2,3; 169.5, C 1,4. IR 2989, 2878, 2644, 2522, 1750, 1717, 1450, 1390, 1383, 1336, 1267, 1216, 1100, 1081, 1027, 899, 847, 712, 690, 656, 621, 565, 464 cm^{-1}. Mass spectrum: *m/z* (as the dimethyl ester) 303, 301, 299 (M–OMe, 1, 2, 1%), 275, 273, 271 (M–(OMe+CO), 1, 2, 1), 253, 251 (M–Br, 5, 5), 225 (10), 223 (10), 221, 219 (M–(MeOH+Br), 35, 37), 209 (7), 207 (7), 193, 191 (M–(MeOH+CO+Br), 18, 19), 172 (M–2Br, 1), 163 (7), 161 (8), 141 (10), 140 (17), 135 (9), 133 (10), 113 (58), 59 (100), 53 (76), 43 (33), 41 (55), 39 (33).

The Anhydride (10)

Diacid (9) (0.15 g) in acetyl chloride (6 mL) was refluxed (2 h). A drying tube (calcium chloride) was then connected to the flask and the solvent allowed to evaporate over 48 h at room temperature. Residual acetyl chloride was then removed under vacuum, and the product sublimed (0.03 mmHg, 50°C, Kugelrohr) to give anhydride (10) (121 mg, 86%). *meso* (2*R*,3*S*)-*2,3-Dibromo-2,3-dimethylsuccinic anhydride* (10) was a colourless powder, m.p. 118–121°C (sublimed) (Found: C, 25.1; H, 2.0. $C_6H_6Br_2O_3$ requires C, 25.2; H, 2.1%). ^{1}H NMR δ 2.11, s, Me. ^{13}C NMR δ 23.7, two Me; 63.8, C 2,3; 167.2, C 1,4. IR 1874, 1792, 1448, 1392, 1378, 1244, 1220, 1185, 1100, 1086, 1070, 962, 896, 795, 762, 736, 670, 637, 532, 424 cm^{-1}. Mass spectrum: *m/z* 216, 214, 212 (M–C_2O_3, 2, 3, 2%), 163, 161 (M–(Br+CO_2), 66, 64), 135, 133 (M–(C_2O_3+Br), 12, 14), 126 (7), 54 (M–(C_2O_3+2Br), 40), 53 (M–(C_2O_3+HBr+Br), 100), 39 (57).

The Anhydride (12)

Dibromomaleic anhydride (15) was synthesized from maleic anhydride and powdered $AlBr_3$ with bromine (140–160°C under an N_2 atmosphere) by following the literature method.[37] Compound (15) gave needles (ether/hexane), m.p. 118.5–121°C (lit.[38] 118–119°C), b.p.$_{19}$ 122°C (lit.[37] b.p.$_{19}$ 117–127°C) (Found: C, 18.9; H, 0.0. Calc. for $C_4Br_2O_3$: C, 18.8; H, 0.0%). ^{13}C NMR δ 131.9, C 2,3; 164.6, C 1,4; consistent with the literature.[29] IR 1765, 1595, 1280, 1233, 1177, 1154, 971, 916, 827, 721, 684 cm^{-1}; also compatible with the literature.[38] The anhydride was stored over P_2O_5. The material was unstable to TLC analysis; development in methanol/chloroform mixtures (2:1) gave two spots (alkaline permanganate) corresponding to dibromomaleic anhydride (15) and dibromomaleic acid. Repeated recrystallization of compound (15) from ether/hexane mixtures led to hydrolysis.

The same material (15) could also be synthesized from dibromomaleic acid with acetyl chloride and sulfuric acid (conc., 1 drop) after reflux.

Freshly distilled cyclopentadiene (388 mg) and anhydride (15) (1.0 g) in dry toluene (65 mL) were heated (4 h, 100°C). The solvent was then evaporated. The residue was recrystallized (benzene) and then sublimed (0.03 mmHg, Kugelrohr) to yield anhydride (12) (768 mg, 61%) which was stored over P_2O_5. (1*R*,2*S*,3*R*,4*S*)-2,3-Dibromobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (*meso* 2-*exo*,3-*exo*-dibromobicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic anhydride) (12) gave a colourless powder, m.p. 181–185°C (sublimed), 188–189°C (benzene) (lit.[39] 188–190°C) (Found: C, 33.6; H, 1.8. Calc. for $C_9H_6Br_2O_3$: C, 33.6; H, 1.9%). ^{1}H NMR see Tables 2 and 3. ^{13}C NMR see Table 1. IR 2990, 2944, 1847, 1784, 1321, 1261, 1225, 1211, 1142, 986, 950, 936, 854, 797, 758, 741, 721, 692, 678, 499 cm^{-1}. Mass spectrum: *m/z* 244 (9), 243, 241 (M–Br, 94, 86%), 215, 213 (M–(Br+CO), 20, 20), 199, 197 (M–(Br+CO_2), 22, 23), 171, 169 (M–(Br+C_2O_3), 17, 17), 149 (11), 147 (14), 118 (15), 90 (84), 89 (84), 66 (100), 63 (63), 51 (21), 50 (24), 44 (26), 39 (45), 38 (25).

Crystallographic Data for Dibromoanhydride (12)

$C_9H_6Br_2O_3$, *M* 321.96, m.p. 188–189°C, colourless needles from benzene, crystal dimensions 0.84 by 0.78 by 0.04 mm, monoclinic, *a* 6.555(4), *b* 21.577(8), *c* 7.393(5) Å, α 90°, β 112.79(4)°, γ 90°, *V* 964.0(9) Å^3, space group *P*2(1)/*c*, *Z* 4, *F*(000) 616, D_c 2.218 g cm^{-3}, linear absorption coefficient 8.384 mm^{-1}, θ-range for data collection 3.13 to 24.99°, index ranges $-7 \le h \le 0$, $-1 \le k \le 25$, $-7 \le l \le 8$, data/restraints/parameters 1693/0/127, goodness-of-fit on F^2 0.838; final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0480, wR_2 = 0.1160, *R* indices (all data) R_1 = 0.0652, wR_2 = 0.1196, largest difference peak and hole 1.514 and –0.957 e Å^{-3}, extinction method: none.

Data were collected at ca. 293 K. Of the 1956 reflections obtained, 1693 were unique (R_{int} 0.0302). Absorption correction: ψ. Check reflections: 3 every 97. Completeness to θ = 24.99: 99.6%. The structure is depicted in Fig. 1. Bond lengths are listed in Table 4, with bond angles in Table 5.

The Anhydride (13)

Anhydride (12) (247 mg) in dry ethyl acetate (25 mL) was hydrogenated (1 h, atmospheric pressure) with PtO_2 (ca. 25 mg). Filtration followed by sublimation of the crude material (0.03 mmHg, 55°C) afforded anhydride (13) as a colourless solid (188 mg, 76%). The material was stored over P_2O_5.

(1*R*,2*R*,3*S*,4*S*)-2,3-Dibromobicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (*meso* 2-*exo*,3-*exo*-dibromobicyclo[2.2.1]heptane-2-*endo*,3-*endo*-dicarboxylic anhydride) (13) had m.p. 186–192°C (subl.) (lit.[18] 198–200°C) (Found: C, 33.7; H, 2.5. Calc. for $C_9H_8Br_2O_3$: C, 33.4; H, 2.5%). ^{1}H NMR see Tables 1 and 2. The $5_{exo},6_{exo}$ system (δ 1.95) had a width between outside peaks of 22.3 Hz; H7$_b$ (δ 2.47) was a dddt with 14 resolved lines; H1 and H4 (δ 3.09) gave a ddt providing 8 lines with width between outside peaks of 8 Hz. ^{13}C NMR see Table 1. IR 2967, 2889, 1877, 1856, 1795, 1453, 1385, 1286, 1217, 1149, 1125, 1029, 988, 940, 855, 838, 721, 697, 684, 506, 492 cm^{-1}. Mass spectrum: *m/z* 326, 324, 322 (M, 0.2, 0.3, 0.1%), 245, 243 (M–Br, 1, 1), 226 (2), 224 (3), 222 (2), 201, 199 (M–(Br+CO_2), 98, 100), 173, 171 (M–(Br+C_2O_3), 31, 33), 164 (M–2Br, 1), 145 (15), 143 (15), 92 (21), 91 (19), 79 (24), 63 (20).

The Anhydride (14)

Bromine in dichloromethane (10 mL, 0.086 M, 0.86 mmol) was added dropwise to a stirred solution of anhydride (12) (276 mg, 0.86 mmol) in dichloromethane (15 mL). The bromine had decolourized after 2 h. The solvent was evaporated to afford anhydride (14) as an off-white solid (400 mg, 97%) which was > 99% pure by ^{1}H and ^{13}C NMR analysis. The material was stored in the dark over P_2O_5. (1*R*,2*S*,3*R*,4*S*,5*R*,6*S*)-*2,3,5,6-Tetrabromobicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride* (*meso* 2-*exo*,3-*exo*,5-*exo*,6-*exo*-tetrabromobicyclo[2.2.1]heptane-2-*endo*,3-*endo*-dicarboxylic anhydride) (14) gave colourless *blocks*, m.p. 205–207°C (dec.) (benzene) (Found: C, 22.3; H, 1.2. $C_9H_6Br_4O_3$ requires C, 22.4; H, 1.3%). ^{1}H NMR ($CDCl_3$) δ 2.60, dm, H7$_b$; 2.76, dt, H7$_a$; 3.29, t, H1,4; 4.19, d, H5,6; with $J_{7a,7b}$ –12.0 Hz, $J_{4,7a} = J_{1,7a} \approx J_{4,7b} = J_{1,7b}$ 1.4 Hz, $J_{5,7b} = J_{6,7b}$ 2.3 Hz, $J_{4,5} = J_{1,6}$ 0 Hz. ^{1}H NMR [(D_6)acetone] see Tables 2 and 3. ^{13}C NMR ($CDCl_3$) δ 35.2, C7; 47.9, C1,4; 62.5, C5,6; 64.6, C2,3; 164.4, C8,9. ^{13}C [(D_6)acetone] see Table 1. IR 1878, 1794, 1461, 1383, 1289, 1229, 1203, 1180, 1144, 979, 934, 721, 693, 554, 488 cm^{-1}. Mass spectrum: *m/z* 486, 484, 482, 480, 478 (M, 1, 4, 7, 7, 1%), 405, 403, 401, 399 (M–Br, 5, 21, 17, 5), 361, 359, 357, 355 (M–(Br+CO_2), 25, 80, 100, 29), 323, 321, 319 (M–(Br+HBr), 33, 56, 31), 250 (16), 173 (32), 171 (38), 145 (16), 143 (15), 89 (17).

Crystallographic Data for Tetrabromoanhydride (14)

$C_9H_6Br_4O_3$, *M* 481.78, m.p. 203–204°C (benzene), colourless blocks, crystal dimensions 0.20 by 0.50 by 0.60 mm, monoclinic, *a* 9.0388(6), *b* 9.5409(6), *c* 14.0075(9) Å, α 90°, β 90.2040(10)°, γ 90°, *V* 1207.98(13) Å^3, space group *P*2(1)/*c*, *Z* 4, *F*(000) 896, D_c 2.649 g cm^{-3}, linear absorption coefficient 13.313 mm^{-1}, θ-range for data collection 2.25 to 23.32°, index ranges $-10 \le h \le 9$, $-7 \le k \le 10$, $-15 \le l \le 13$, data/restraints/parameters 1724/0/146, goodness-of-fit on F^2 1.012; final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0532, wR_2 = 0.1312, *R* indices (all data) R_1 = 0.0655, wR_2 = 0.1374, largest difference peak and hole 1.793 and –1.620 e Å^{-3}, extinction coefficient 0.0106(9).

Data were collected at ca. 144 K. Of the 4309 reflections obtained, 1724 were unique (R_{int} 0.0676). Absorption correction: semi empirical. Completeness to θ = 23.32: 98.5%. The structure is depicted in Fig. 2. Bond lengths are listed in Table 4, with bond angles in Table 5.

The Decomposition of Anhydride (14) (Diacid 16a)

Attempts to recrystallize anhydride (14) (400 mg) from acetone initially provided pearly leaflets which re-dissolved on standing (overnight, room temperature). Evaporation of the resultant discoloured solution yielded an off-white gum, which was comprised of debrominated diacid (16a) and an unidentified compound (ca. 1:6 by ^{1}H NMR analysis). On further standing (2 days, benchtop), the NMR sample [(D_6)acetone] containing this 1:6 mixture darkened considerably. Re-analysis (^{1}H and ^{13}C NMR) indicated quantitative conversion into the diacid (16a). The crude product was insoluble in chloroform and could not be sublimed.

The anhydride (14) (40 mg) in (D_6)acetone (ca. 1 mL) in an NMR tube was allowed to stand in the light. Periodic analyses (^{1}H NMR) indicated a slow conversion of compound (14) into the unidentified compound and the diacid (16a) (ca. 70:20:10, respectively, after three days; 40:30:30 after six days; 10:30:60 after eight days). After 14 days the mixture was comprised solely of diacid (16a) (100%; pure by ^{1}H and ^{13}C NMR analysis). The corresponding dimethyl ester (16b) (methanol/sulfuric acid) gave a single peak by GCMS analysis. The unidentified component could not be purified.

(1*R*,4*S*,5*S*,6*R*)-*5,6-Dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic acid* (*meso* 5-*exo*,6-*exo*-dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic acid) (16a) gave irregular prisms, m.p. 266–267°C (water) (Found: C, 31.4; H, 2.2. $C_9H_8Br_2O_4$ requires C, 31.8; H, 2.4%). ^{1}H NMR see Tables 2 and 3. ^{13}C NMR see Table 1. IR 3456, 2989, 2911, 2644, 2489, 1699, 1627, 1580, 1450, 1354, 1299, 1258, 1142, 1101, 1026, 913, 882, 838, 817, 776, 764, 754, 622, 537, 474, 410 cm^{-1}.

(1*R*,4*S*,5*S*,6*R*)-*Dimethyl 5,6-dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate* (*meso* dimethyl 5-*exo*,6-*exo*-dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate) (16b), an oil, was identical (^{1}H and ^{13}C NMR, MS, IR) with the material obtained from the bromination of compound (20b) as described below.

The unidentified compound [possibly structure (17)] was too unstable to isolate. It had the following data [abstracted from mixtures also containing compounds (14) and (16a)]. ^{1}H NMR δ 2.69, dt, *J* –11.5, 1.4 Hz, 1H; 2.81, dm, *J* –11.5, 2.2, 1.4 Hz, 1H; 3.19, t, *J* 1.4, 1.4 Hz, 2H; 4.84, d, *J* 2.2 Hz, 2H. ^{13}C NMR δ 34.5, 65.0, 71.9, 138.1, 169.0.

Dibromide (19)

Bromination (CCl_4, under normal laboratory fluorescent lighting) of anhydride (18) gave (1*R*,2*S*,3R,4*S*,5*S*,6*R*)-5,6-dibromobicyclo-[2.2.1]heptane-2,3-dicarboxylic anhydride (*meso* 5-*exo*,6-*exo*-dibromobicyclo[2.2.1]heptane-2-*endo*,3-*endo*-dicarboxylic anhydride) (19) (90% yield) as needles from benzene, m.p. 206–209°C (lit.[40,41] 206°C, 209–210°C) (Found: C, 33.1; H, 2.4. Calc. for $C_9H_8Br_2O_3$: C, 33.4; H, 2.5%). NMR [(D_6)acetone]: see Tables 1–3. IR (Nujol mull) 1865, 1783, 1306, 1075, 944, 909 cm^{-1}. Mass spectrum: *m/z* 326 (2%), 324 (M, 5), 322 (2), 245 (M–Br, 36), 243 (36), 186 (13), 173 (25), 171 (25), 147 (12), 145 (11), 91 (82), 66 (C_5H_6, 100) 39 (48).

Crystallographic Data for Dibromoanhydride (19)

$C_9H_8Br_2O_3$, *M* 323.97, m.p. 206–209°C (benzene), colourless needles, crystal dimensions 0.85 by 0.20 by 0.13 mm, monoclinic, *a* 12.314(9), *b* 6.730(5), *c* 12.966(9) Å, α 90°, β 115.80(3)°, γ 90°, V 967.4(12) Å^3, space group *P*2(1)/*c*, *Z* 4, *F*(000) 624, D_c 2.224 g cm^{-3}, linear absorption coefficient 8.355 mm^{-1}, θ-range for data collection 3.16 to 25.00°, index ranges $-14 \le h \le 3$, $0 \le k \le 8$, $-14 \le l \le 14$, data/restraints/parameters 1677/0/117, goodness-of-fit on F^2 0.830; final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0324, wR_2 = 0.0634, *R* indices (all data) R_1 = 0.0596, wR_2 = 0.0662, largest difference peak and hole 0.540 and –0.522 e Å^{-3}, extinction coefficient 0.0106(9).

Data were collected at 144(2) K. Of the 2117 reflections obtained, 1677 were unique (R_{int} 0.040). Absorption correction: semi empirical. Completeness to θ = 25.00: 98.8%. Intensities of three standard reflections, measured every 97 reflections throughout the data collection, showed only negligible decay. Hydrogen atoms were fixed in geometrically calculated positions and treated as riding. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. The structure is depicted in Fig. 3, with bond lengths listed in Table 4 and bond angles in Table 5.

Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid (20a)

Hydrochloric acid (conc., 15 mL) was added to the monopotassium salt of acetylene dicarboxylic acid (10 g) in water (90 mL). Freshly distilled cyclopentadiene (23.15 g) was added and the mixture was stirred vigorously for 4 h. The mixture containing a white precipitate was extracted into chloroform and the solvent removed. The crude material was dissolved in aqueous sodium hydroxide and the mixture washed with chloroform. The aqueous layer was acidified (conc. hydrochloric acid, pH 2) to give a white precipitate. The mixture was extracted into dichloromethane, dried (magnesium sulfate), and evaporated to give the title diacid (20a) (5.45 g, 46% yield), m.p. 165–167°C (lit.[42,43] 163–164°C, 170°C). ^{1}H and ^{13}C NMR were consistent with the literature,[42] with $J_{1,5} = J_{4,6}$ 1.6 Hz, $J_{1,6} = J_{4,5}$ 2.4 Hz, $J_{1,7a} = J_{4,7a}$ 1.5 Hz, $J_{1,7b} = J_{4,7b}$ 1.6 Hz, $J_{5,7a} = J_{6,7a}$ 0.3 Hz, $J_{5,7b} = J_{6,7b}$ 0.4 Hz, $J_{7a,7b}$ 7.1Hz. IR (hexachlorobutadiene mull) 3300–2200, 2950, 2881, 2490, 1698, 1585, 1462, 1222, 706 cm^{-1}.

Dimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (20b)

Compound (20a) (0.31 g) in methanol (60 mL) containing sulfuric acid (conc., 1 mL) was stirred (24 h), at which time analysis (GCMS) showed that complete methylation of both acid groups had occured. Methanol was removed. Dichloromethane (100 mL) was added and the mixture was washed with saturated sodium bicarbonate solution (2 × 20 mL) and water. Drying (magnesium sulfate) and removal of the dichloromethane gave the dimethyl ester (20b) as a colourless oil (0.35 g, 98% yield) (lit.[22] pale yellow oil). This material was used without further purification. ^{1}H NMR ($CDCl_3$) consistent with the literature;[44] with $J_{1,5} = J_{4,6}$ 1.7 Hz, $J_{1,6} = J_{4,5}$ 2.2 Hz, $J_{1,7a} = J_{4,7a}$ 1.4 Hz, $J_{1,7b} = J_{4,7b}$ 1.5 Hz, $J_{5,7a} = J_{6,7a}$ 0.3 Hz, $J_{5,7b} = J_{6,7b}$ 0.4 Hz, $J_{7a,7b}$ 6.8Hz. ^{13}C NMR ($CDCl_3$) δ 51.7, two OMe; 53.2, C1,4; 72.7, C7; 142.1, C5,6; 152.2, C2,3; 165.1, C8,9. IR (neat) 3629, 3552, 3420, 3126, 3071, 3000, 2950, 2873, 2844, 1717, 1626, 1559, 1435, 1364, 1293, 1201, 1150, 1100, 1055, 1019, 952, 918, 869, 832, 779, 758, 734, 714 cm^{-1}. Mass spectrum: *m/z* 208 (M, 19%), 193 (16), 177 (38), 176 (43), 161 (20), 149 (61), 133 (11), 119 (32), 118 (36), 105 (26), 90 (59), 77 (45), 66 (100), 59 (58), 51 (26), 39 (62).

Bromination of Dimethyl Ester (20b)

Bromine (0.11 g) in dichloromethane (5 mL) was added to a stirred solution of diester (20b) (0.13 g) in dichloromethane (50 mL). The reaction flask was sealed and left to stir for 8 h under standard fluorescent lighting. Analysis (GC) showed at least five products, with no starting material. The solvent was removed under reduced pressure to give a viscous oil (0.21 g). Excess bromine was removed on a small silica column (hexane/ethyl acetate, 4:1).

Flash column chromatography (hexane/ether, 83:17), followed by normal-phase HPLC (hexane/ethyl acetate, 9:1) gave samples of the five products, all as colourless, viscous oils. All the dibromides except compound (16b) (*meso*) are assumed to be racemic. The products in order of increasing polarity were the following.

(1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,6*SR*)-*Dimethyl-3,5-dibromotricyclo[2.2.1.0^{2,6}]heptane-2,3-dicarboxylate* (dimethyl 3-*exo*,5-*exo*-dibromotricyclo[2.2.1.0^{2,6}]heptane-2-*endo*,3-*endo*-dicarboxylate) (23) (HPLC relative retention 1.00) (Found: C, 35.8; H, 3.3. $C_{11}H_{12}Br_2O_4$ requires C, 35.9; H, 3.3%). ^{1}H NMR ($CDCl_3$) δ 2.29, ddt, H1; 2.40, dt, H7a; 2.56, dt, H6; 2.57, dddd, H7b; 2.60, br sextet, H4; 3.69 and 3.79, two s, OMe; 4.00, dt, H5; with $J_{1,4}$ 1.4 Hz, $J_{1,6}$ 5.1 Hz, $J_{1,7a} \sim J_{1,7b}$ 1.3 Hz, $J_{4,5}$ 1.5 Hz, $J_{4,6}$ 1.4 Hz, $J_{4,7a}$ 1.3 Hz, $J_{4,7b}$ 1.5 Hz, $J_{5,6}$ 1.4 Hz, $J_{5,7b}$ 0.6 Hz, $J_{7a,7b}$ 12.1 Hz. ^{13}C NMR ($CDCl_3$) δ 26.4, C1; 31.8, C6; 32.1, C7; 36.2, C2; 47.2, C5; 49.7, C4; 52.0 and 53.5, two OMe; 62.1, C3; 168.0 and 168.2, two CO; with $J_{C1,H1}$ 183.1 Hz, $J_{C4,H4}$ 159.6 Hz, $J_{C5,H5}$ 162.9 Hz, $J_{C6,H6}$ 188.1 Hz, $J_{C7,H7a} \sim J_{C7,H7b}$ 141.0 Hz, $J_{C10,H10}$ 148.3 Hz, $J_{C11,H11}$ 147.6 Hz. IR (paraffin mull) 1745, 1724, 1440, 1329, 1301, 1280, 1255, 1235, 1200, 1170, 1137, 1132, 1114, 1061, 1054, 1029, 1002, 988, 971, 886, 798, 783, 767, 739 cm^{-1}. Mass spectrum: (Kratos) *m/z* 369.9075, 367.9084, 365.9112; $C_{11}H_{12}{}^{81}Br_2O_4$ requires 369.9064, $C_{11}H_{12}{}^{79}Br^{81}BrO_4$ requires 367.9084, $C_{11}H_{12}{}^{79}Br_2O_4$ requires 365.9103. GCMS: *m/z* 339 (3%), 337 (M–31, 6), 335 (3), 311 (3), 309 (7), 307 (3), 289 (90), 287 (100), 257 (39), 255 (31), 229 (16), 227 (18), 207 (17), 149 (15), 148 (15), 91 (11), 90 (14), 89 (20), 59 (24).

(1*RS*,2*SR*,3*RS*,4*SR*,5*SR*,6*SR*)-*Dimethyl 3,5-dibromotricyclo[2.2.1.0^{2,6}]heptane-2,3-dicarboxylate* (dimethyl 3-*endo*,5-*exo*-dibromotricyclo[2.2.1.0^{2,6}]heptane-2-*exo*,3-*exo*-dicarboxylate) (24) (relative retention 1.25) (Found: C, 35.9; H, 3.4. $C_{11}H_{12}Br_2O_4$ requires: C, 35.9; H, 3.3%). ^{1}H NMR ($CDCl_3$) δ 1.67, ddt, H7b; 2.20, dt, H7a; 2.37, d of br q, H1; 2.47, dt, H6; 2.58, br sextet, H4; 3.69 and 3.77, two s, OMe; 4.82, dt, H5; with $J_{1,4}$ 1.3 Hz, $J_{1,6}$ 5.2 Hz, $J_{1,7a}$ 1.4 Hz, $J_{1,7b}$ 1.5 Hz, $J_{4,5}$ 1.5 Hz, $J_{4,6}$ 1.4 Hz, $J_{4,7a} \approx J_{4,7b}$ 1.5 Hz, $J_{5,6}$ 1.5 Hz, $J_{5,7b}$ 0.6 Hz, $J_{7a,7b}$ 12.3 Hz. ^{13}C NMR ($CDCl_3$) δ 25.9, C1; 28.9, C7; 31.5, C6; 35.9, C2; 49.2, C4; 52.2, C5; 52.0 and 53.4, two OMe; 62.9, C3; 167.3 and 168.1, two CO; with $J_{C1,H1}$ 184.8 Hz, $J_{C4,H4}$ 160.6 Hz, $J_{C5,H5}$ 166.9 Hz, $J_{C6,H6}$ 187.4 Hz, $J_{C7,H7a}$ and $J_{C7,H7b}$ 139.0 and 140.0 Hz, respectively, $J_{C10,H10}$ 148.1 Hz, $J_{C11,H11}$ 147.5 Hz. IR (neat) 2954, 2852, 1742, 1736, 1439, 1435, 1373, 1301, 1282, 1258, 1239, 1209, 1162, 1131, 1114, 1058, 1036, 920, 765, 740 cm^{-1}. Mass spectrum: (Kratos) *m/z* 369.9054, 367.9079, 365.9103; $C_{11}H_{12}{}^{81}Br_2O_4$ requires 369.9064, $C_{11}H_{12}{}^{79}Br^{81}BrO_4$ requires 367.9084, $C_{11}H_{12}{}^{79}Br_2O_4$ requires 365.9103. GCMS: *m/z* 370 (1%), 368 (M, 2), 366 (1), 339 (4), 337 (8), 335 (5), 311 (6), 309 (11), 307 (6), 290 (14), 289 (100), 287 (93), 257 (47), 255 (46), 229 (16), 227 (18), 207 (64), 176 (22), 149 (26), 148 (20), 105 (19), 91 (18), 90 (24), 89 (34), 77 (19), 63 (23), 59 (41).

(1*RS*,4*SR*,5*SR*,6*SR*)-*Dimethyl-5,6-dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate* (dimethyl 5-*exo*,6-*endo*-dibromobicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate) (21) (relative retention 1.59) (Found: C, 37.8; H, 3.8. $C_{11}H_{12}Br_2O_4$ requires C, 35.9; H, 3.3%).* ^{1}H NMR ($CDCl_3$) δ 2.12, dddd, H7b; 2.18, dt, H7a; 3.41, d of br q, H4; 3.64, ddt, H1; 3.71 and 3.83, two s, OMe; 4.06, dt, H5; 4.48, dd, H6; with $J_{1,4}$ 1.8 Hz, $J_{1,6}$ 3.6 Hz, $J_{1,7a}$ 1.3, $J_{1,7b}$ 2.0 Hz, $J_{4,5}$ 0.6 Hz, $J_{4,7a}$ 1.4 Hz, $J_{4,7b}$ 1.6 Hz, $J_{5,6}$ 2.7 Hz, $J_{5,7b}$ 2.6 Hz, $J_{7a,7b}$ 10.2 Hz. ^{13}C NMR ($CDCl_3$) δ 45.7, C7; 52.2 and 52.3, two OMe; 52.2, C1; 52.8, C5; 54.2, C6; 55.4, C4; 141.9 and 144.9, C2 and C3, respectively; 162.8 and 164.4, two CO; with $J_{C1,H1}$ 157.0 Hz, $J_{C4,H4}$ 157.2 Hz, $J_{C5,H5}$ 170.5 Hz, $J_{C6,H6}$ 165.2 Hz, $J_{C7,H7a}$ and $J_{C7,H7b}$ 138.0 and 139.0 Hz, respectively, $J_{C10,H10}$ 147.8 Hz, $J_{C11,H11}$ 147.6 Hz. IR (neat) 2952, 1722, 1630, 1450, 1436, 1345, 1280, 1244, 1194, 1172, 1152, 1130, 1088, 1014, 976, 823, 784, 749 cm^{-1}. Mass spectrum: (Kratos) *m/z* 367.9094; $C_{11}H_{12}{}^{79}Br^{81}BrO_4$ requires 367.9084. Mass spectrum: (Finnigan) *m/z* 368.9150; $C_{11}H_{13}{}^{79}Br^{81}BrO_4$ (M+H) requires 368.9155. GCMS: *m/z* 370 (3%), 368 (M, 4), 366 (2), 339 (7), 337 (13), 335 (7), 311 (1), 309 (2), 307 (1), 289 (14), 287 (12), 257 (37), 255 (31), 183 (12), 182 (100), 151 (14), 150 (8), 149 (10), 148 (8), 119 (9), 105 (8), 89 (14), 79 (23), 59 (24).

(1*R*,4*S*,5*S*,6*R*)-Dimethyl 5,6-dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (*meso* dimethyl 5-*exo*,6-*exo*-dibromobicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate) (16b) (relative retention 1.84) (Found: C, 37.2; H, 3.6. $C_{11}H_{12}Br_2O_4$ requires C, 35.9; H, 3.3%).* ^{1}H NMR ($CDCl_3$) see Tables 2–3, with $J_{1,6endo} = J_{4,5endo}$ 0 Hz. ^{13}C NMR ($CDCl_3$) see Table 1, with $J_{C1,H1} = J_{C4,H4}$ 157.1 Hz, $J_{C5,H5} = J_{C6,H6}$ 166.5 Hz, $J_{C7,H7a}$ and $J_{C7,H7b}$ 138.3 and 139.0 Hz, respectively, $J_{C10,H10} = J_{C11,H11}$ 147.9 Hz. IR (paraffin mull) 1725, 1629, 1337, 1261, 1196, 1156, 1134, 1091, 1026, 976, 886, 838, 784, 757 cm^{-1}. Mass spectrum: (Kratos) *m/z* 369.9249, 367.9092, 365.9095; $C_{11}H_{12}{}^{81}Br_2O_4$ requires 369.9064, $C_{11}H_{12}{}^{81}Br^{79}BrO_4$ requires 367.9084, $C_{11}H_{12}{}^{79}Br_2O_4$ requires 365.9103. GCMS: *m/z* 370 (1%), 368 (M, 2), 366 (1), 339 (4), 337 (10), 335 (5), 289 (7), 287 (7), 257 (21), 255 (17), 183 (12), 182

*Despite giving correct NMR and HRMS data these samples consistently provided microanalyses high in both carbon and hydrogen.

(100), 151 (21), 150 (10), 149 (10), 119 (10), 93 (15), 89 (15), 79 (28), 59 (28).

(1*RS*,4*RS*,5*SR*,7*RS*)-*Dimethyl 5,7-dibromobicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate* (dimethyl 5-*exo*,7-*anti*-dibromobicyclo[2.2.1]-hept-2-ene-2,3-dicarboxylate) (22) (relative retention 1.94) (Found: C, 35.3; H, 3.3. $C_{11}H_{12}Br_2O_4$ requires: C, 35.9; H, 3.3%). ^{1}H NMR ($CDCl_3$) δ 2.28, dddd, H6$_{endo}$; 2.71, ddd, H6$_{exo}$; 3.36, dddd, H1; 3.59, dd, H4; 3.77 and 3.78, two s, OMe; 3.88, dd, H5; 4.15, br pentuplet, H7b; with $J_{1,4}$ 1.8 Hz, $J_{1,6endo}$ 0.7 Hz, $J_{1,6exo}$ 3.6 Hz, $J_{1,7b}$ 1.5 Hz, $J_{4,5}$ 0 Hz, $J_{4,7b}$ 1.5 Hz, $J_{5,6endo}$ 8.1 Hz, $J_{5,6exo}$ 4.5 Hz, $J_{5,7b}$ 1.4 Hz, $J_{6endo,6exo}$ 13.5 Hz, $J_{6endo,7b}$ 1.3 Hz. ^{13}C NMR ($CDCl_3$) δ 33.6, C6; 41.6, C5; 51.9, C1; 52.5 and 52.5, two OMe; 54.2, C7; 56.8, C4; 142.2 and 144.3, C2 and C3, respectively; 162.3 and 163.0, two CO; with $J_{C1,H1}$ 155.1 Hz, $J_{C4,H4}$ 160.3 Hz, $J_{C5,H5}$ 164.5 Hz, $J_{C6,H6}$ 139.0 and 141.0 Hz, respectively, $J_{C7,H7b}$ 167.2 Hz, $J_{C10,H10}$ 148.1 Hz, $J_{C11,H11}$ 147.9 Hz. IR (neat) 3000, 2953, 2848, 1733, 1731, 1622, 1435, 1337, 1287, 1223, 1202, 1155, 1135, 1113, 1090, 1046, 1004, 965, 919, 888, 867, 839, 817, 796, 779, 764, 726 cm^{-1}. Mass spectrum: (Kratos) *m/z* 369.9015, 367.9089, 365.9110; $C_{11}H_{12}{}^{81}Br_2O_4$ requires 369.9064, $C_{11}H_{12}{}^{81}Br^{79}BrO_4$ requires 367.9084, $C_{11}H_{12}{}^{79}Br_2O_4$ requires 365.9103. GCMS: *m/z* 368 (M, < 1%), 339 (16), 337 (33), 335 (15), 290 (9), 289 (64), 287 (70), 262 (10), 260 (9), 258 (11), 257 (100), 255 (81), 229 (23), 227 (20), 207 (13), 201 (8), 176 (9), 175 (13), 173 (12), 172 (8), 171 (11), 170 (8), 153 (8), 151 (9), 150 (9), 149 (30), 148 (30), 133 (9), 122 (12), 121 (11), 119 (32), 105 (27), 91 (33), 90 (29), 89 (44), 78 (21), 77 (35), 65 (23), 63 (42), 59 (69), 39 (37).

Dibromoanhydride (*25*)

Anhydride (19) (or its corresponding dibasic acid) was heated with a small amount of water in a glass tube (230°C, Woods' metal bath). Water vapour and hydrogen bromide were evolved in the early part of the reaction. Equilibrium appeared to be reached after 2 h between anhydride (19) and anhydride (25) (1:4 by ^{1}H NMR). The cooled mixture was taken into ethyl acetate, washed with aqueous sodium carbonate and water, then dried (magnesium sulfate) to afford a crystalline mixture. Recrystallization (acetonitrile, 2×) gave (1*R*,2*S*,3*R*,4*S*,5*S*,6*R*) 5,6-dibromobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride (25) (*meso* 5-*exo*,6-*exo*-dibromobicyclo-[2.2.1]hepta-2,5-diene-2-*exo*,3-*exo*-dicarboxylic anhydride) (yield 45%), m.p. 252–254°C (lit.[9,45] 248–249°C, 244–245°C). NMR see Tables 1–3. IR (Nujol) 1844, 1782, 1086, 951, 903, 606 cm^{-1}. Mass spectrum: *m/z* 326, 324, 322 (M, 3, 7, 3%), 245, 243 (M–Br, 41, 37), 173 (26), 171 (28), 91 (81), 66 (100), 39 (40).

When anhydride (19) was heated under strictly anhydrous conditions no rearrangement to anhydride (25) was observed. Both starting material (19) and product (25) decomposed under prolonged heating.

Dibromides (27) and (28)

Dibromides (27) and (28) were synthesized by standard procedures,[46] and separated and purified by preparative GC. Each compound (a colourless oil) gave consistent spectral data and provided a single peak by GCMS analysis, with *trans*-dibromide eluting first.

syn-*Bromination Trials*

Cyclohexene was distilled and stored under argon prior to use. *Syn*-bromination experiments were carried out by dissolving anhydride (10), (13) or (14) (1–2 mg, ca. 0.002–0.003 mmol) in either cyclohexene (1 mL), or mixtures (1:1) of cyclohexene (0.5 mL) and either benzene, methanol, chloroform, acetone or 1,4-dioxan (0.5 mL). Trials were then performed under a range of conditions:

a. The sample was refluxed under argon in diffuse light, and the mixtures analysed at one, two and five hour intervals.

b. The sample was directly irradiated with a 100 W bulb overnight.

c. The sample was stored in the presence of sunlight, and analysed after approx. one week.

d. The sample was placed both in the dark, and in diffuse light, and left to stand for prolonged periods (weeks) at room temperature.

For stability tests, the starting anhydrides (10), (13) and (14) and the dibromides (27) and (28) were subjected to the same conditions as outlined above. Analyses were performed using GC and/or GCMS (Alltech EC-5 capillary column) using a temperature gradient of 80–5–16–270, an injector temperature of 220°C and a detector temperature of 250°C. No product (27) was observed in any trial. The by-products formed had the library mass spectra: 3-bromocyclohexene (*m/z*) 162, 160 (M, 1, 1%), 82 (8), 81 (M–Br, 100), 79 (31), 66 (5), 65 (5), 53 (18), 52 (7), 51 (10), 41 (14), 39 (19); 2-bromocyclohexanol (*m/z*) 180, 178 (M, 1, 1%), 137 (1), 135 (1), 134 (4), 132 (3), 122 (1), 121 (1), 99 (M–Br, 27), 82 (7), 81 (100), 79 (11), 69 (5), 67 (3), 57 (64), 55 (15), 43 (17), 41 (30), 39 (24).

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