(*R*)-1,3-Dimethylcyclopropene—One Isomer of the Smallest Chiral Hydrocarbon

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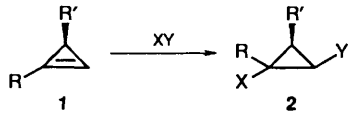
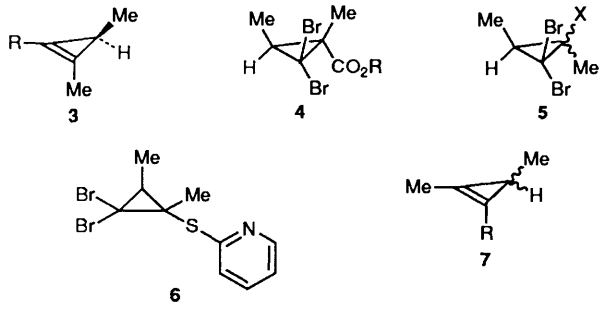
1-Lithio-1,3-dimethylcyclopropene has been obtained in optically active form in five steps from tiglic acid and trapped with electrophiles to produce, among others, optically active 1,3-dimethylcyclopropene.

There has been considerable recent interest in the use of cyclopropenes in synthesis.[1] As a part of our own studies in this area, we wished to develop simple routes to chiral cyclopropenes such as **1**, addition of XY to which would, in principle, lead to three chiral centres, as in **2**.



Scheme 1

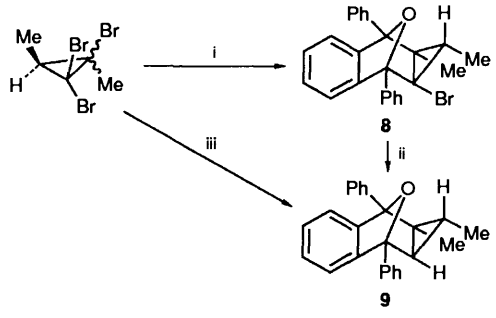
We now report a route to an enantiomerically pure 1-bromocyclopropene **3** (R = Br), and the corresponding 1-lithiospecies **3** (R = Li), and its application in the preparation of 1,3-dimethylcyclopropene **3** (R = H) as a single enantiomer.



Reaction of *tert*-butyl tiglate† with bromoform and aqueous sodium hydroxide in the presence of cetrimide led to the cyclopropane **4** (R = Bu^t) (65%) which was converted into the corresponding acid **4** (R = H)[2] (87%) by treatment with trifluoroacetic acid. This acid could be resolved by treatment with either pseudoephedrine or quinine; in the former case the (+)-acid was obtained after crystallisation of the salt formed with (−)-pseudoephedrine and regeneration of the acid, and treatment of the acid regenerated from the mother liquors with (+)-pseudoephedrine then led to the (−)-acid. In the case of quinine, the (+)-acid was obtained. The optical purity of the resolved acid was determined by conversion into the corresponding acid chloride and reaction of this with (+)-(*R*)-α-methylbenzylamine when the ^{1}H NMR signals of the two diastereoisomeric amides could be distinguished.

Reaction of racemic acid **4** (R = H) with lead tetraacetate[3] or red mercuric oxide and bromine[4] in carbon tetrachloride gave 1,1,2-tribromo-2,3-dimethylcyclopropane **5** (X = Br); a mixture of stereoisomers about C-2 was obtained as is normal for such reactions.[5] In the same way reaction of **4** (R = H) with lead tetraacetate and lithium chloride[6] led to the corresponding chloride **5** (X = Cl), while lead tetraacetate and iodine[7] gave the unstable iodide **5** (X = I) as a mixture of two isomers in ratio 1:2.2. Attempted bromodecarboxylation of the acid chloride of **4** (R = H) with *N*-hydroxypyridine-2-thione in bromotrichloromethane[8] led to the sulfide **6**.

Reaction of racemic cyclopropane **5** (X = Br) with methyllithium in ether led to 1-bromo-2,3-dimethylcyclopropene **7** (R = Br) (82%), which could be flash distilled and observed directly by ^{1}H NMR and trapped as an adduct **8** with 1,3-diphenylisobenzofuran. Treatment of **5** (X = Br) with 2 mol



Scheme 2 *Reagents*: i, (a) MeLi (1 mol equiv.), (b) 1,3-diphenylisobenzofuran; ii, Li–Bu^{t}OH–THF; iii, (a) MeLi (2 mol equiv.), (b) H_2O, (c) 1,3-diphenylisobenzofuran

equiv. of methyllithium, followed by removal of all the volatiles at 0.5 mmHg gave a white solid, presumed to contain the lithiocyclopropene **7** (R = Li);[9] addition of water through a septum generated the parent 1,3-dimethylcyclopropene[10] which was swept into a cooled receiver by a stream of nitrogen. The product was not completely separated from traces of residual ether, but the distilled yield was estimated as 47%; this should be regarded as a minimum in view of experimental difficulties on the scale used. If **5** (X = Br) was treated with 2 mol equiv. of methyllithium in ether and the products were treated directly with gaseous carbon dioxide, the acid **7** (R = CO_2H) was obtained.

When the above experiments were repeated with the tribromide **5** (X = Br) obtained from optically active dibromo-acid **4** (R = H), the optically active acid **3** (R = CO_2H), bromide **3** (R = Br) and hydrocarbon **3** (R = H) were obtained. The optical purity of the acid was determined by treatment with (+)-(*R*)-α-methylbenzylamine. The ^{1}H NMR of the derived salt in the region of 3-Me of the cyclopropane showed a doublet; the corresponding region of the spectrum of salt derived from racemic acid showed two doublets of equal size. In order to establish the stereochemistry of the latter two compounds they were trapped by reaction with 1,3-diphenyl-

† Tiglic acid = (*E*)-2-methylbut-2-enoic acid or (*E*)-2-methylcrotonic acid.

Table 1 Atomic coordinates (× 10^4) for compound **8**

	x	*y*	*z*
Br	3905.5(5)	6410.4(6)	2907.6(2)
O	1531(3)	5158(3)	4332.5(13)
C(1)	4537(6)	3046(6)	3323(2)
C(2)	3480(5)	3870(5)	3698(2)
C(3)	3136(5)	5419(5)	3577(2)
C(4)	4008(5)	5038(4)	4109(2)
C(5)	5583(5)	5398(6)	4194(2)
C(6)	2934(5)	5470(5)	4603(2)
C(7)	2920(5)	7116(5)	4591(2)
C(8)	3627(5)	8139(5)	4917(2)
C(9)	3472(6)	9579(5)	4755(2)
C(10)	2649(6)	9953(6)	4279(3)
C(11)	1974(6)	8906(5)	3932(2)
C(12)	2114(5)	7482(5)	4091(2)
C(13)	1693(5)	6042(5)	3809(2)
C(14)	405(5)	5904(5)	3415(2)
C(15)	−722(5)	6887(5)	3422(2)
C(16)	−1909(5)	6711(6)	3060(2)
C(17)	−1986(5)	5551(6)	2675(2)
C(18)	−864(6)	4558(5)	2666(2)
C(19)	328(5)	4743(5)	3026(2)
C(20)	3073(5)	4739(5)	5189(2)
C(21)	2296(6)	5272(5)	5667(2)
C(22)	2420(6)	4631(6)	6216(2)
C(23)	3291(6)	3431(5)	6288(2)
C(24)	4049(7)	2873(5)	5813(2)
C(25)	3920(6)	3531(5)	5267(2)

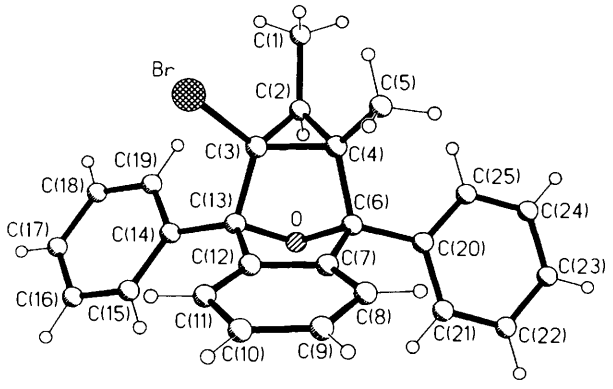


Fig. 1 X-Ray molecular structure of a single enantiomer of compound **8**

isobenzofuran; the X-ray crystal structure of the optically active bromo-adduct **8** was determined and the absolute stereochemistry is shown (Fig. 1). The atomic coordinates and selected bond lengths and angles for **8** are given in Tables 1 and 2. This establishes the absolute stereochemistry of (+)-**4** as (1*S*,2*S*) (as shown in the diagram) and of the derived cyclopropenes **3** (R = H, Br, CO_2H) (again as shown in the diagram). It is important to note also the stereochemistry about the ring junction, which is in agreement with those reported for other cyclopropene Diels–Alder products,[11,12] and the stereochemistry of 3-Me of the cyclopropene. Reduction of the bromide with lithium–*tert*-butanol–tetrahydrofuran (THF) gave[13] **9** which was identical to that obtained directly from 1,3-dimethylcyclopropene.

Although the preparation of specific optically active cyclopropenes has been reported,[14] and the preparation of optically pure 1,3-dimethylcyclopropene is primarily of academic interest, the above method does in principle allow ready access to a range of 1,3-dialkylcyclopropenes in optically pure form. This, and the chemistry of the products are under examination.

Table 2 Selected bond lengths (Å) and angles (°) for compound **8**

Br–C(3)	1.916(4)	C(1)–C(2)	1.506(7)
C(2)–C(3)	1.498(6)	C(2)–C(4)	1.513(6)
C(3)–C(4)	1.498(6)	C(3)–C(13)	1.547(7)
C(4)–C(5)	1.506(7)	C(4)–C(6)	1.552(6)
C(3)–C(2)–C(1)	121.4(4)	C(3)–C(2)–C(4)	59.7(3)
C(1)–C(2)–C(4)	120.4(4)	C(4)–C(3)–C(2)	70.7(3)
C(4)–C(3)–C(13)	105.9(4)	C(2)–C(3)–C(13)	118.6(4)
C(4)–C(3)–Br	123.9(3)	C(2)–C(3)–Br	121.9(3)
C(13)–C(3)–Br	114.4(3)	C(3)–C(4)–C(5)	124.9(4)
C(3)–C(4)–C(2)	59.7(3)	C(5)–C(4)–C(2)	123.4(4)
C(3)–C(4)–C(6)	100.5(4)	C(5)–C(4)–C(6)	117.9(4)
C(2)–C(4)–C(6)	115.3(4)		

Experimental

Organic solutions were dried ($MgSO_4$), and solvents were removed at 14 mmHg. Column chromatography was performed using Merck Kieselgel 60; TLC was carried out using Kieselgel 60 F 254 Aluminium plates. M.p.s were carried out on a Kofler hot stage apparatus and are uncorrected. IR spectra were recorded using a Nicolet 20 SXB FTIR spectrometer. Mass spectra were obtained from an A.E.I. M.S.9 or Kratos M.S. 80 R.F. spectrometer, operating at 70 eV. ^1H NMR spectra were recorded in deuteriochloroform using a Varian EM 360, a Hitachi Perkin-Elmer R-24B or a Bruker AC 250 or WM 300-WB spectrometer (tetramethylsilane was used as the internal standard). *J*-Values are given in Hz. Microanalyses were performed with a Carlo-Erba Instrumentazione model 1106 CHN analyser. GLC was performed using a Packard 427 GC containing a 10 m SE 30 quartz capillary column.

Ether was dried ($CaCl_2$) followed by distillation from lithium aluminium hydride; dichloromethane was dried by distillation over phosphorus pentoxide; tetrahydrofuran was distilled over lithium aluminium hydride; light petroleum was the fraction with b.p. 40–60 °C.

Esterification of (E)-2-*Methylbut-2-enoic Acid with Isobutylene.*—Isobutylene (*ca.* 40 cm^3) was condensed into a Schlenk tube containing (*E*)-2-methylbut-2-enoic acid (10 g, 0.1 mol) at −78 °C. Sulfuric acid (0.5 cm^3) was added and the vessel sealed and placed in a shaker. After 3 days at room temperature the vessel was cooled to −78 °C before opening and allowing excess isobutylene to escape. The reaction was worked up by neutralising with sodium hydrogen carbonate and extracting with ether (2 × 200 cm^3). The volatiles were removed to leave *tert*-butyl (*E*)-2-methylbut-2-enoate (14.2 g, 91%); $\delta_H(CDCl_3)$ 6.45 (1 H, q, *J* 11), 1.82 (3 H, s), 1.70 (3 H, d, *J* 11) and 1.4 (1 H, br s).

Reaction of tert-*Butyl* (E)-2-*Methylbut-2-enoate with Bromoform and Base under Phase Transfer Conditions.*—Sodium hydroxide (10.7 g, 270 mmol) in water (25 cm^3) was added over a period of 5 min to a rapidly stirred solution of *tert*-butyl (*E*)-2-methylbut-2-enoate (14.2 g, 90 mmol), cetrimide (0.4 g) and bromoform (45.4 g, 180 mmol). The reaction was stirred vigorously for 48 h at 50 °C, then worked up by diluting with water (250 cm^3) and extracting with dichloromethane (3 × 100 cm^3); the combined organic extracts were dried and the solvent removed to give a thick yellow oil which was distilled at 80–82 °C/0.1 mmHg and identified as *tert*-butyl 2,2-dibromo-1,3-dimethylcyclopropanecarboxylate **4** (R = Bu^t), (19 g, 65%) (Found: M^+, 326.0623. $C_{10}H_{16}Br_2O_2$ requires *M*, 326.0628); $\delta_H(CDCl_3)$ 2.15 (1 H, q, *J* 7), 1.45 (9 H, br s), 1.3 (3 H, s) and 1.1 (3 H, d, *J* 7); *m/z* 326, 269, 253, 247 and 225.

Hydrolysis of Carboxylate **4** (R = Bu^t).—The ester (20 g, 68 mmol) was hydrolysed by heating to 80 °C with trifluoroacetic

acid (15 cm^3) for 2 h. When TLC showed that no further ester was present, the reaction was worked up by careful addition of saturated sodium hydrogen carbonate solution until no further effervescence occurred. The aqueous layer was then re-acidified to pH 1 with 10% HCl then re-extracted with dichloromethane (3 × 100 cm^3). The combined organic layers were dried and the solvent removed to yield a white crystalline solid which was purified by recrystallising from light petroleum and identified as 2,2-dibromo-1,3-dimethylcyclopropanecarboxylic acid **4** (R = H) (14 g, 87%), m.p. 85–87 °C (Found: C, 26.4; H, 3.1. $C_6H_8Br_2O_2$ requires: C, 26.48; H, 2.96%); $\delta_H(CDCl_3)$ 8.78 (1 H, br s), 2.25 (1 H, q, *J* 7), 1.3 (3 H, s) and 1.1 (3 H, d, *J* 7); $\delta_C(CDCl_3)$ 177.1, 39.6, 37.0, 32.8, 15.0 and 12.1; ν_{max}(KBr disc)/cm^{-1} 3100, 1690, 1440 and 1200; *m/z* 270, 252 and 224.

Resolution of Acid **4** (R = H).—(a) *With pseudoephedrine.* A hot solution of cyclopropanecarboxylic acid **4** (R = H) (26 g, 96 mmol) in chloroform (150 cm^3) was added to a solution of (−)-pseudoephedrine (15.9 g, 96 mmol) in chloroform. The solution was allowed to stand for 45 min at room temperature before filtering off the precipitated salt {5.3 g; free acid $[\alpha]_D$ +37 (*c* 0.2, $CHCl_3$)}. Recrystallisation from chloroform (22 cm^3) and methanol (1 cm^3) gave salt {4.1 g; free acid $[\alpha]_D$ +48 (*c* 0.2, $CHCl_3$)}. A second recrystallisation from chloroform (20 cm^3) and methanol (1 cm^3) gave the salt {2.6 g; free acid $[\alpha]_D$ +57 (*c* 0.2, $CHCl_3$)}; further recrystallisation did not increase the rotation.

A second batch of crystals was obtained from the original mother liquor, and after three recrystallisations from chloroform–methanol, 1.6 g of salt was precipitated. The free acid of this was found to have a rotation of +54.

The solvent was removed from the combined mother liquors to leave the partially resolved salt (35 g). The free acid was regenerated by dissolving the salt in chloroform and washing thoroughly with HCl (3 × 100 cm^3). The recovered acid (19.5 g, 72 mmol) was then dissolved in chloroform and added to a solution of (+)-pseudoephedrine (11.9 g, 72 mmol). Two recrystallisations of the first precipitated salt {6 g, $[\alpha]_D$ −40 (*c* 0.2, $CHCl_3$) for free acid} gave 2.7 g of salt whose corresponding acid had a rotation of −59 (*c* 0.3, $CHCl_3$). Further recrystallisation did not change the m.p. or the rotation.

(b) *With quinine.* A hot solution of quinine (29 g, 89 mmol) in acetonitrile (100 cm^3) and methanol (10 cm^3) was added to a hot solution of carboxylic acid **4** (R = H) (24 g, 89 mmol) in acetonitrile (100 cm^3). After 35 min the precipitated salt {19.6 g, $[\alpha]_D$ −78 (*c* 0.1, $CHCl_3$)} was filtered off and recrystallised from acetonitrile and methanol (10:1). Two further recrystallisations gave the salt {2.3 g, $[\alpha]_D$ −69 (*c* 0.1, $CHCl_3$)}, further recrystallisation of which did not increase the $[\alpha]_D$ value. The acid was regenerated by dissolving in chloroform and washing thoroughly with 10% HCl. The volatiles were removed to leave the acid which was recrystallised from methanol {1.1 g, $[\alpha]_D$ +54 (*c* 0.1, $CHCl_3$)}, m.p. 86–88 °C (Found: C, 26.4; H, 3.0. $C_6H_8Br_2O_2$ requires: C, 26.48; H, 2.96%); $\delta_H(CDCl_3)$ 8.78 (1 H, br s), 2.25 (1 H, q, *J* 7), 1.3 (3 H, s) and 1.1 (3 H, d, *J* 7).

A second crop of crystals was filtered from the mother liquor; after three recrystallisations from acetonitrile and methanol the free acid was regenerated as described previoulsy {0.9 g, $[\alpha]_D$ +57 (*c* 0.1, $CDCl_3$)}. All spectral data were identical with that above.

2,2-*Dibromo*-1,3-*dimethylcyclopropanecarbonyl Chloride.*—(a) To a solution of carboxylic acid **4** (1 g, 3.68 mmol) in dry benzene (10 cm^3) was added oxalyl chloride (0.90 cm^3, 3.7 mmol) and DMF (0.1 cm^3). On addition of the DMF the solution effervesced vigorously and stirring was continued until the reaction subsided. The volatiles were removed at 14 mmHg to leave the title acid chloride, yellow oil (1.05 g, 98%), which was used without further purification; $\delta_H(CDCl_3)$ 2.42 (1 H, q, *J* 6), 1.58 (3 H, s) and 1.3 (3 H, d, *J* 6).

(b) Thionyl chloride (0.5 cm^3) was added to the acid (0.5 g, 1.85 mmol) in a thoroughly dried flask under a nitrogen atmosphere. The resulting solution was stirred at room temperature for 18 h before removing excess thionyl chloride by distillation (14 mmHg, 25 °C). The acid chloride was then distilled at 0.4 mmHg, 50–55 °C and used without further purification.

2,2-*Dibromo*-1,3-*dimethyl*-N-(α-*methyl*)*benzylcyclopropanecarboxamide.*—(a) *From acid chloride.* To a solution of the acid chloride in CCl_4 (2 cm^3) was added (+)-(*R*)-α-methylbenzylamine (0.1 cm^3, 0.82 mmol). After refluxing for 45 min and cooling, the solution was diluted with dichloromethane and washed with sodium hydrogen carbonate (2 cm^3). Removal of the volatiles left a pale yellow solid which was purified by recrystallisation from CCl_4 and identified as the title carboxamide (0.11 g, 53%) (Found: M^+, 372.9671. $C_{14}H_{17}Br_2NO$ requires *M*, 372.9672); $\delta_H(CDCl_3)$ (mixture of diastereoisomers) 7.3 (5 H, m), 6.01 (1 H, br s), 5.17 (1 H, q, *J* 7.2), 2.36 (1 H, q, *J* 6.6), 2.33 (1 H, q, *J* 6.6), 1.55 (3 H, d, *J* 7), 1.37 (3 H, s), 1.34 (3 H, s), 1.16 (3 H, d, *J* 6.6) and 1.165 (3 H, d, *J* 6.6); *m/z* 373, 358 and 294.

(b) *From optically pure acid* ($[\alpha]_D$ −59). The amide was prepared by the method described above (Found: M^+, 372.9678. $C_{14}H_{17}Br_2NO$ requires *M*, 372.9672); $\delta_H(CDCl_3)$ 7.3 (5 H, m,), 5.17 (1 H, q, *J* 7.2), 2.35 (1 H, q, *J* 6.6), 1.56 (3 H, d, *J* 6.9), 1.37 (3 H, s) and 1.16 (3 H, d, *J* 6.6); *m/z* 373, 358 and 294.

(c) *From optically pure acid* ($[\alpha]_D$ +57). The amide was prepared by the previously described method (Found: M^+, 372.9677. $C_{14}H_{17}Br_2NO$ requires *M*, 372.9672); $\delta_H(CDCl_3)$ 7.3 (5 H, m), 6.16 (1 H, br), 5.13 (1 H, q, *J* 7), 2.32 (1 H, q, *J* 6.6), 1.52 (3 H, d, *J* 7), 1.31 (3 H, s) and 1.12 (3 H, d, *J* 6.6); *m/z* 373, 358 and 294.

1,2,2-*Tribromo*-1,3-*dimethylcyclopropane* **5**.—(a) Bromine (0.3 g, 0.93 mmol) was carefully added to a refluxing suspension of acid **4** (R = H) (0.5 g, 1.85 mmol) and red mercuric oxide (0.4 g, 1.85 mmol) in carbon tetrachloride. The reaction was refluxed for 90 min before cooling and the suspension was filtered. The filtrate was washed with 5% NaOH (3 cm^3) and then water (3 cm^3) before being dried and the volatiles removed to leave a pale yellow oil which was purified by distillation at 60–62 °C/0.3 mmHg and identified as cyclopropane **5** (X = Br) (0.39 g, 69%), identical by NMR and GLC to an authentic sample (Found: M^+, 303.8100. $C_5H_7Br_3$ requires *M*, 303.8102); $\delta_H(CDCl_3)$ 1.96 (1 H, q, *J* 6.6), 1.87 (3 H, s) and 1.22 (3 H, d, *J* 6.6); $\delta_C(CDCl_3)$ 42.7, 42.5, 38.7, 24.0 and 11.92; ν_{max}(cap. film)/cm^{-1} 2978, 2930, 1446 and 1386; *m/z* 304, 289 and 225.

(b) Bromine was slowly added to a refluxing suspension of title acid (0.25 g, 0.92 mmol) and lead tetraacetate (0.4 g, 0.92 mmol) in dry carbon tetrachloride (10 cm^3). The reaction was illuminated with a tungsten lamp until no further bromine was consumed. The reaction was worked up by allowing to cool and then washing with 5% perchloric acid (2 cm^3) followed by aqueous sodium hydrogen carbonate (5 cm^3). The organic layer was then dried and the solvent removed to yield a pale yellow oil which was purified by distillation and identified as **5** (X = Br) (0.21 g, 73%). All spectral data were identical with the above compound.

Optically pure cyclopropane **5** (X = Br). The above described reaction was repeated using optically pure acid (1.5 g) (1.2 g, 71%). GLC revealed the presence of two isomers in a ratio of 1:2.9 {$[\alpha]_D$ +6.6 (*c* 0.2, $CHCl_3$)}.

Decarboxylative Chlorination of Carboxylic Acid **4** (R = H).—Lead tetraacetate (1.67 g, 3.78 mmol) was added to a

solution of title acid (1.05 g, 3.86 mmol) in benzene (5 cm^3) under a nitrogen atmosphere. The mixture was stirred at room temperature until homogeneous before adding lithium chloride (01.6 g, 3.8 mmol). The apparatus was flushed with nitrogen before refluxing for 35 min after which time no further yellow colouration remained. The organic layer was decanted from the residue and the residue washed with ether. The combined organic layers were washed with dilute perchloric acid (3 cm^3) then sodium carbonate (3 cm^3) before drying ($MgSO_4$). The volatiles were removed to leave a pale yellow oil which was purified by column chromatography eluting with light petroleum and identified as 2,2-dibromo-1-chloro-1,3-dimethylcyclopropane **5** (X = Cl) (500 mg, 49%). GC analysis revealed the presence of two isomers in a ratio of 1:3.9 which could not be separated; $\delta_H(CDCl_3)$ (major) 1.92 (1 H, q, *J* 6.6), 1.72 (3 H, s) and 1.22 (3 H, d, *J* 6.6); (minor) 1.94 (3 H, s), 1.61 (1 H, q, *J* 6.4) and 1.29 (3 H, d, *J* 6.4); *m/z* 227 and 181.

Photochemical Decarboxylative Iodination of Carboxylic Acid **4** (R = H).—Iodine (0.47 g, 1.85 mmol) was added to a refluxing suspension of title acid (0.5 g, 1.85 mmol) and lead tetraacetate (0.81 g, 1.85 mmol) in CCl_4 (10 cm^3) under a nitrogen atmosphere. The mixture was illuminated with a tungsten lamp and refluxed until the iodine colour was no longer present. The cooled suspension was filtered and the filtrate washed with sodium hydrogen carbonate solution (5 cm^3) and then water (5 cm^3). The volatiles were removed from the dried organic layer to leave a pale yellow solid which was identified as 1,1-dibromo-2-iodo-2,3-dimethylcyclopropane **5** (X = I) (0.45 g, 69%). GC analysis revealed the presence of two isomers in the ratio of 1:2.2. This was also confirmed by NMR; $\delta_H(CDCl_3)$ (major) 2.01 (3 H, s), 1.75 (1 H, q, *J* 6.6) and 1.18 (3 H, d, *J* 6.6); (minor) 2.29 (3 H, s), 1.27 (3 H, d, *J* 6.6) and 0.79 (1 H, q, *J* 6.6); ν_{max}(KBr disc)/cm^{-1} 2975, 2928, 1736, 1439 and 747; *m/z* 273, 227 and 194. The product was unstable hence an elemental analysis was not possible.

Attempted Decarboxylative Chlorination of Carboxylic Acid **4** (R = H) *with* N-*Hydroxypyridine-2-thione*.—1,3-Dimethyl-2,2-dibromocyclopropanecarbonyl chloride (0.5 g, 1.73 mmol) in carbon tetrachloride (10 cm^3) was carefully added over 15 min to a refluxing solution of *N*-hydroxypyridine-2-thione, sodium salt (0.31 g, 2.1 mmol) and dimethylaminopyridine (DMAP) (20 mg) in CCl_4 (20 cm^3). The reaction was monitored by TLC; when this showed no further starting material remained the reaction was allowed to cool. Work-up was achieved by washing the organic layer with water (2 × 5 cm^3), then brine (5 cm^3). The organic layer was dried and the solvent removed to yield a yellow oil which was purified by column chromatography, eluting with light petroleum and ether (6:1). The oil solidified on standing to yield a pale yellow crystalline solid which was identified as 2,2-dibromo-1,3-dimethylcyclopropyl 2-pyridyl sulfide **6** (0.42 g, 72%) (Found: M^+, 334.8980. $C_{10}H_{11}Br_2NS$ requires *M*, 334.8976); NMR spectroscopy indicated the presence of two isomers in a 4:1 ratio; $\delta_H(CDCl_3)$ (major) 8.4 (1 H, m), 7.55 (1 H, m), 7.22 (1 H, m), 7.02 (1 H, m), 1.84 (1 H, q, *J* 6.4), 1.66 (3 H, s) and 1.28 (3 H, d, *J* 6.4); (minor) 8.4 (1 H, m), 7.55 (1 H, m), 7.22 (1 H, m), 7.02 (1 H, m), 1.87 (3 H, s), 1.72 (1 H, q, *J* 6.50) and 1.32 (3 H, d, *J* 6.50); $\delta_C(CDCl_3)$ (mixture) 158.7, 158.1, 149.7, 136.5, 122.1, 119.9, 46.3, 46.1, 38.0, 37.0, 36.2, 35.8, 27.0, 19.2, 14.0 and 12.0; *m/z* 336, 256 and 177.

Attempted Decarboxylative Bromination of Carboxylic Acid **4** (R = H).—The acid chloride (0.5 g, 1.73 mmol) in bromotrichloromethane (10 cm^3) was added over 15 min to a refluxing suspension of *N*-hydroxypyridine-2-thione sodium salt (0.31 g, 2.46 mmol) and DMAP (20 mg) in bromotrichloromethane (20 cm^3). The reaction was monitored by TLC and when no further starting material remained the cooled suspension was filtered through Celite. The filtrate was dried and the volatiles removed to yield a pale yellow solid which was purified by column chromatography eluting with light petroleum and ether. The pale yellow crystalline solid was identified as **6** (0.38 g, 64%). GLC showed two isomers in a 4:1 ratio, all other spectral data was identical to that above.

Treatment of Cyclopropane **5** (X = Br) *with Methyllithium*.—Methyllithium (1.04 cm^3, 1.56 mmol, 1.2 mol equiv.) was carefully added to a solution of title cyclopropane (0.4 g, 1.3 mmol) in dry ether (5 cm^3) at −80 °C. The reaction was allowed to warm to room temperature and stirred for 10 min before being cooled to −40 °C and quenched with water (1 cm^3). The ether was decanted from ice and the ice washed with ether (2 cm^3) and the procedure repeated. The ether was removed from the combined organic layers at −30 °C/0.1 mmHg and the product purified by distillation (10 °C/0.3 mmHg) and identified as 1-bromo-2,3-dimethylcyclopropene **7** (R = Br) (82%, 0.17 g); $\delta_H(CDCl_3)$ 2.05 (3 H, s), 2.03 (1 H, q, *J* 5.45) and 1.1 (3 H, d, *J* 5.45). The compound decomposed during a ^{13}C NMR accumulation, hence further analysis was impossible. However, confirmation of its structure was gained in a subsequent trapping experiment.

Treatment of Cyclopropane **5** (X = Br) *with Methyllithium followed by Electrophilic Substitution with Water*.—Methyllithium (4.1 mmol, 2.7 cm^3) was added to a stirred solution of title cyclopropane (0.5 g, 1.6 mmol) in dry ether (10 cm^3) at −78 °C under nitrogen. The mixture was allowed to reach 20 °C and stirred for a further 30 min before being cooled to −50 °C and the ether removed under reduced pressure. When only a fine white powder remained the flask was flushed with nitrogen, and water (1 cm^3) was added *via* a septum, and the product was then distilled at −30 °C/0.1 mmHg. The 250 MHz ^1H NMR spectrum of the distillate showed the desired compound had formed, but the cyclopropene **7** (R = H) (estimated yield 50 mg, 47%) could not be completely separated from ether. A substantial amount of product may have been lost during the removal of ether, hence the actual yield was higher than 47%; $\delta_H(CDCl_3)$ 6.5 (1 H, br s), 1.91 (3 H, s), 1.90 (1 H, q, *J* 4.8) and 0.97 (3 H, d, *J* 4.8).

1,3-*Dimethylcyclopropenecarboxylic Acid* **7** (R = CO_2H).—Methyllithium (2.7 cm^3, 4.1 mmol) was carefully added to a solution of racemic cyclopropane **5** (X = Br) (0.5 g, 1.6 mmol) in dry ether at −78 °C. The solution was allowed to reach 0 °C and stirred at this temperature for 10 min before being cooled to −50 °C. A rapid stream of CO_2 was then bubbled through for 20 min before the reaction was allowed to reach room temperature and a slow stream of CO_2 maintained for a further 10 min. The mixture was then cooled to −40 °C and quenched with water (2 cm^3). After allowing to reach room temperature, the aqueous layer was acidified and extracted with ether (3 × 5 cm^3). The ether layers were combined and dried and the ether removed at 14 mmHg to yield a pale yellow oil which was identified as the title acid **7** (R = CO_2H) (210 mg, 46%) (Found: M^+, 112.0525. $C_6H_8O_2$ requires *M*, 112.0522); $\delta_H(CDCl_3)$ 10.8 (1 H, br s), 2.35 (3 H, s), 1.97 (1 H, q, *J* 4.8) and 1.17 (3 H, d, *J* 4.8); *m/z* 112 (M^+) and 67 ($M^+ - CO_2H$); ν_{max}(KBr disc)/cm^{-1} 2961, 1836 and 1680.*

* The acid **7** (R = CO_2H) is unstable and in the absence of solvent rapidly dimerises by an ene-reaction (J. R. Al Dulayymi and M. S. Baird, unpublished results).

Addition of (+)-(R)-α-Methylbenzylamine to Racemic Carboxylic Acid **7** (R = CO_2H).—(+)-(*R*)-α-Methylbenzylamine (31 mg, 0.26 mmol) was added to a solution of racemic carboxylic acid **7** (R = CO_2H) (30 mg, 0.26 mmol) in deuterochloroform (0.7 cm^3) at 0 °C. The solution was allowed to reach room temperature and a spectrum was run immediately; this clearly showed the salt had been formed; δ_H(200 MHz, $CDCl_3$) 7.3 (5 H, m), 4.1 (2 H, br q, *J* 7.3), 1.94 (3 H, s), 1.50 (1 H, q, *J* 4.6), 1.36 (3 H, d, 6.7) and 0.91 (3 H, d, *J* 4.6). Expansion of the δ 0.91–1.1 region confirmed the presence of two very close doublets at δ 0.91 due to the two enantiomeric salts.

Addition of (+)-(R)-α-Methylbenzylamine to Optically Active Carboxylic Acid **3** (R = CO_2H).—(+)-(*R*)-α-Methylbenzylamine (31 mg, 0.26 mmol) was added to a solution of optically active carboxylic acid **3** (R = CO_2H) (30 mg, 0.26 mmol) [prepared as above but from optically active cyclopropane **5** (X = Br)] in deuteriochloroform (0.7 cm^3) at 0 °C. The solution was allowed to reach room temperature and a spectrum was run immediately; δ_H(200 MHz, $CDCl_3$) 7.3 (5 H, m), 4.1 (2 H, br q, *J* 7.3), 2.03 (3 H, s), 1.54 (1 H, q, *J* 4.6), 1.40 (3 H, d, *J* 6.5) and 0.99 (3 H, d, *J* 4.6). Expansion of the δ 0.91–1.1 region confirmed the presence of only one doublet, hence optically pure cyclopropenecarboxylic acid had been obtained.

Preparation and Trapping of Chiral 1,3-*Dimethylcyclopropene.*—Methyllithium (9.6 cm, 14.5 mmol, 2.2 mol equiv.) was added dropwise to a solution of optically pure cyclopropane **5** (X = Br) (2.0 g, 6.6 mmol) in dry ether (5 cm^3) at −80 °C under nitrogen. The reaction temperature was then allowed to reach 20 °C where it was kept for 40 min before cooling to −40 °C; the ether was then removed at −20 °C under reduced pressure to yield a white powder. The apparatus was then flushed with nitrogen into a receiver flask which contained a solution of 1,3-diphenylisobenzofuran (1.77 g, 6.58 mmol) in dry ether (*ca.* 5 cm^3) and was placed in liquid nitrogen. Water (1.5 cm^3) was then carefully added through a septum to the white powder at −30 °C and the gaseous 1,3-dimethylcyclopropene allowed to distil into the cold receiver. A colour change in the trap from bright yellow to intense lime green was observed as this occurred. After 10 min at liquid nitrogen temperature the solution of diphenylisobenzofuran and cyclopropene was allowed slowly to reach room temperature and stirred under nitrogen for 2 h. The organic layer was washed with water and dried and the volatiles removed to leave a pale straw coloured solid. After recrystallisation from light petroleum and ether the solid was identified as 10,11-dimethyl-1,8-diphenyl-12-oxatetracyclo[6.3.1.$0^{2,7}$.$0^{9,11}$]dodeca-2,4,6-triene **9** (1.2 g, 54%), m.p. 104–106 °C {$[\alpha]_D$ +11.85 (*c* 0.45, $CDCl_3$)} (Found: C, 88.5; H, 6.3. $C_{25}H_{22}O$ requires: C, 88.72; H, 6.55%); δ_H($CDCl_3$) 7.73 (4 H, complex multiplet), 7.5–7.0 (10 H, complex multiplet), 2.43 (1 H, dq, *J* 6.6, 3.2), 1.30 (3 H, d, *J* 6.7), 1.16 (1 H, d, *J* 3.2) and 1.15 (3 H, s); δ_C($CDCl_3$) 14 aromatic signals, 91.5, 88.4, 38.3, 33.8, 29.7, 24.9, 13.2 and 10.9; ν_{max}/cm^{-1} 3032, 1661, 1594, 1497, 1448 and 749.

Preparation and Trapping of Optically Active Cyclopropene **3** (R = Br).—Methyllithium (3.93 cm^3, 5.9 mmol, 1.1 mol equiv.) was added to a solution of optically active cyclopropane **5** (X = Br) (1.51 g, 4.89 mmol) in dry ether (7.5 cm^3) at −80 °C. The solution was allowed to warm to room temperature and stirred for 40 min before cooling to −40 °C and quenching with water (1.5 cm^3). The ether was decanted from the ice and 1,3-diphenylisobenzofuran (1.0 g, 3.7 mmol) was added. After stirring for 4 h at room temperature, the ether solution was washed with water, dried and evaporated to give a cream coloured solid. This was recrystallised from light petroleum and ether and characterised as 9-bromo-10,11-dimethyl-1,8-diphenyl-12-oxatetracyclo[6.3.1.$0^{2,7}$.$0^{9,11}$]dodeca-2,4,6-triene **8** (1.3 g, 84%), m.p. 120–122 °C {$[\alpha]_D$ 33.2 (*c* 0.5, $CDCl_3$)} (Found: C, 71.7; H, 5.1. Calc. for $C_{25}H_{21}BrO$: C, 71.95; H, 5.07%); δ_H 7.6 (18 H, complex multiplet), 2.30 (1 H, q, *J* 6.7), 1.45 (3 H, d, *J* 6.7) and 1.15 (3 H, s); δ_C 14 aromatic signals plus 91.1, 91.0, 57.5, 34.8, 28.0, 12.9 and 10.17; ν_{max}/cm^{-1} 3030, 1498, 1458, 1300, 983 and 750.

Reduction of Bromocyclopropane.—To a stirred solution of optically pure **8** (0.2 g, 0.48 mmol) in dry THF (1 cm^3) and *tert*-butanol (0.7 cm^3) under a nitrogen atmosphere was added lithium powder (30 mg). The suspension was refluxed for 72 h before cooling and carefully quenching the reaction with ice–water (2 cm^3). The product was extracted with ether (3 × 2 cm^3) and the combined organic layers washed with brine (2 cm^3). The volatiles were removed to leave compound **9** (0.15 g, 82%) which was purified by recrystallising from carbon tetrachloride. All spectral data were identical to those of the authentic sample above {$[\alpha]_D$ +11.5 (*c* 0.47, $CDCl_3$)}, m.p. 104–106 °C.

Crystallography.—Crystal data for **8**. $C_{25}H_{21}BrO$, M_r = 417.3, orthorhombic, *a* = 9.242(2), *b* = 9.282(2), *c* = 22.766(5) Å, *V* = 1953.0(7) $Å^3$ (from 2θ values of 32 reflections measured at ±ω, 30 < 2θ < 40°), *Z* = 4, D_c = 1.419 g cm^{-3}, *F*(000) = 856, λ(Cu-Kα) = 1.541 84 Å, μ = 294 mm^{-1}, space group $P2_12_12_1$, *T* = 160.0(10) K.

Data collection and processing. Stoe-Siemens diffractometer with Cryostream cooler,[15] crystal size 0.58 × 0.58 × 0.27 mm, ω/θ scan mode with on-line profile fitting,[16] $2\theta_{max}$ 130°, index ranges *h* 0 to 10, *k* 0 to 10, *l* 0 to 26, together with a complete set of Friedel opposites and a few equivalent reflections, negligible variation of intensity for five standard reflections, semiempirical absorption correction from ψ-scans (transmission 0.119–0.280); 2149 reflections measured, 1924 unique, R_{int} = 0.0721.

Structure solution and refinement.[17] Direct methods, full-matrix least-squares refinement on F^2 for all data, weighting $w^{-1} = \sigma^2(F_0^2) + (0.1044P)^2 + 1.18P$, where $P = (F_0 + 2F_c)/3$, insignificant extinction effects; anisotropic displacement parameters, scattering factors from ref. 18, constrained H atoms with isotropic thermal parameters, $wR^2 = [\Sigma w(F^2_0 - F^2_c)/\Sigma wF^2_0]^{1/2}$ = 0.1221, conventional *R* = 0.0462 based on *F* values for 1919 reflections with $F^2_0 > 2\sigma(F^2_0)$, goodness of fit 1.038, final difference electron density within ±0.92 $eÅ^{-3}$. The absolute configuration was unambiguously established by refinement of the Flack *x* parameter[19] to 0.02(3).

Full lists of bond lengths and angles and of atomic displacement parameters are available as supplementary material from the CCDC.*

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* For details of the crystallographic deposition scheme, see 'Instructions for Authors (1993)', *J. Chem. Soc., Perkin Trans. 1*, 1993, issue.

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