The Stereochemical Course of the Photochemical Berson-Willcott Rearrangement of *exo*-1-Methoxycarbonylmethyl-3-*t*-butyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene to 7-Methoxycarbonylmethyl-5-*t*-butyl-7*H*-benzocycloheptene

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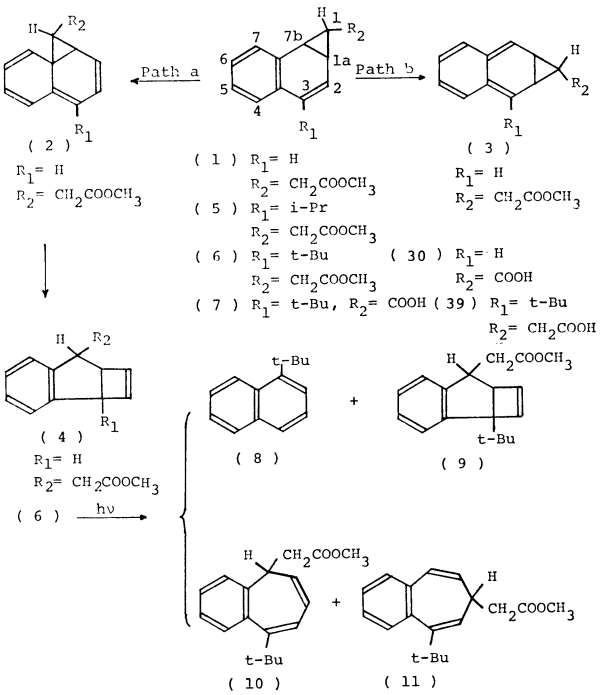
The photolysis of (1*S*)-*exo*-1-methoxycarbonylmethyl-3-*t*-butyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene gave (7*S*)-5-*t*-butyl-7-methoxycarbonylmethyl-7*H*-benzocycloheptene by a 1,5-sigmatropic shift, proving the rearrangement to proceed with the inversion of the configuration of the migrating center.

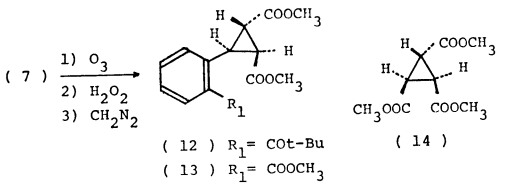
The photochemical Berson-Willcott rearrangement of 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes has been studied by Pomerantz,[1] Swenton,[2,3] and by us.[4-6] The rearrangement has thus been clarified to proceed *via* two 1,5-shift intermediates[2,3,6] (*e.g.* **2** and **3**).

In the earlier communication,[4] we clarified the rearrangement of methoxycarbonylmethyl derivative (**1**) along the path i proceeded *via* a mechanism with inversion of the configuration of C-1. Because of the molecular symmetry of **3**, it was impossible to establish the stereochemical course of path ii by using this starting material, and accordingly we chose 3-substituted derivative of **1** as a starting material. In a previous paper, we reported the photochemistry of 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes (**5**) substituted with an isopropyl group at the C-3. In the present study we investigated the photolysis of the *t*-butyl homologue (**6**), with a hope to obtain much larger amount of an unsymmetrical rearrangement product of the path ii,[7] which would allow us to establish the stereochemistry of the reaction.

The starting acid, 3-*t*-butyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-*exo*-carboxylic acid (**7**) was prepared from 1-*t*-butylnaphthalene (**8**) through the reaction with ethyl diazoacetate in the presence of copper powder. The acid **7** was transformed by Arndt-Eistert reaction to the next higher homologue (**6**), which was found to be thermally stable below 100 °C.[8] The methyl ester **6** in methanol was photolysed with the aid of a high pressure mercury arc (UM-452) through a Pyrex filter. The products were, in addition to **8** and a small amount of a cyclobut[*a*]indene (**9**) (*exo* : *endo*= 1 : 1), a 5*H*-benzocycloheptene (**10**) and a 7*H*-benzocycloheptene (**11**).[7]



Scheme 1.



Scheme 2.

The acid **7** was carefully resolved into optically active components *via* its brucine salt. The absolute configuration of (+)-**7** was established as (1*R*) by ozonization, oxidative cleavage of the ozonide and subsequent esterification of the product with diazomethane. Of three products, (**12**—**14**), **13** was identical with a sample of known stereochemistry, (1*S*,2*S*)-3-[*o*-(methoxycarbonyl)phenyl]-1,2-bis(methoxycarbonyl)cyclopropane.[4] The optical purity of **7** was estimated, after transformation to its methyl ester, by NMR measurement with use of a chiral shift reagent, tris[3-(2,2,3,3,-4,4,4-heptafluoro-1-hydroxybutylidene)-*d*-camphorato]-europium(III). In the NMR spectra, the racemic ester showed two proton signals for the methoxycarbonyl group in equal intensities, but the (+)-ester showed one strong signal without accompanying signal more intense than 5% of the main one (Fig. 1).

The independent photolysis of each optically active ester **6** under the same conditions as described above gave the optically active esters, **9**, **10**, and **11** as shown in Table 1.

The 7*H*-benzocycloheptene, (+)-**11**, $[\alpha]_D$+127°, was hydrogenated over 10% Pd-C to give (−)-dihydro derivative (**15**), $[\alpha]_D$−61.2°, which was oxidized with purple benzene and was esterified to give a (+)-keto diester (**16**), $[\alpha]_D$+16°. In the same way, (−)-**11**, $[\alpha]_D$−89.9°, was transformed to (−)-**16**, $[\alpha]_D$−15.6°.

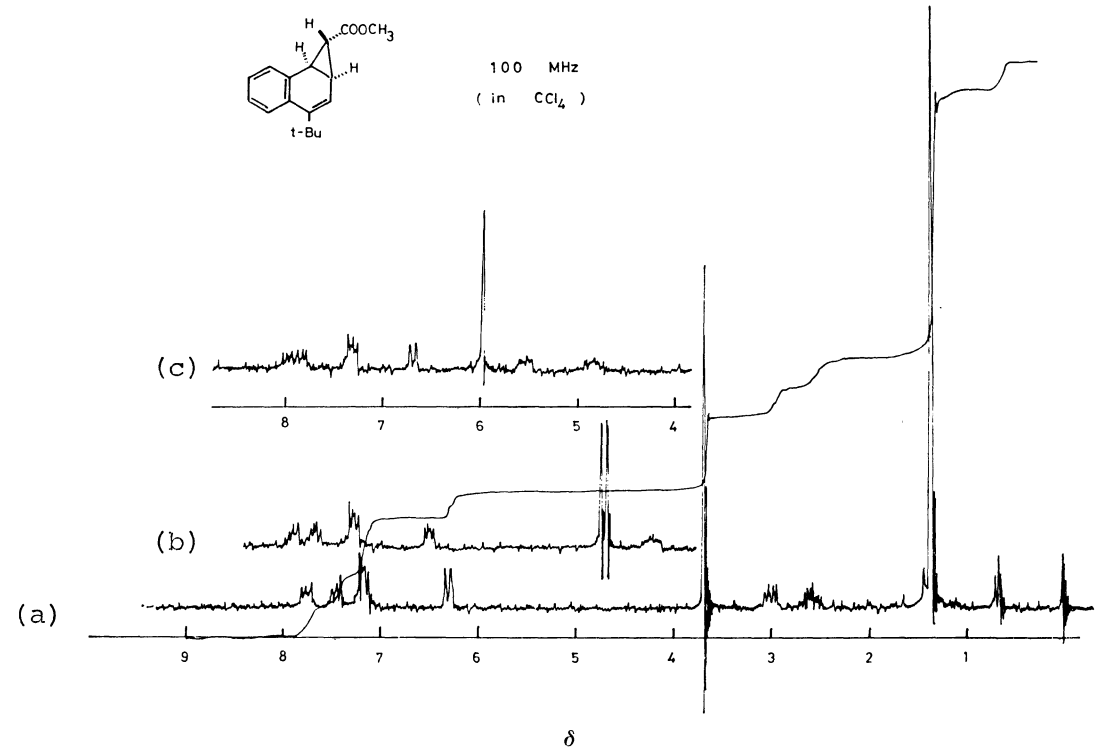
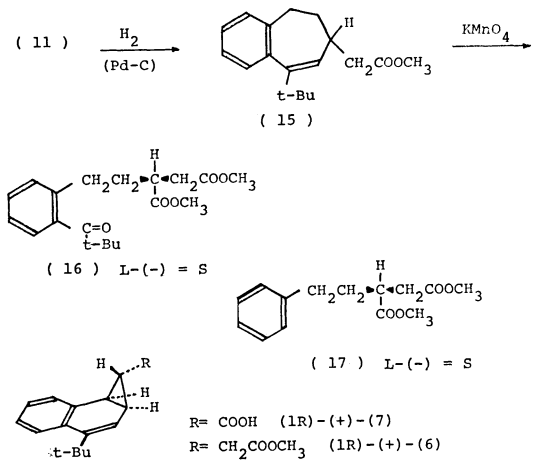


Fig. 1. ^{1}H NMR spectra of the methyl ester of **7**.
(a) Original spectrum of the racemic ester, (b) after addition of a chiral shift reagent to the above ester, (c) after addition of a chiral shift reagent to the optically active ester, obtained from (+)-acid **7**, $[\alpha]_D = +14.3°$.

Table 1. Specific rotation relationships between optically active ester **6** and the photolysis products

Starting materials		Products			
Acid **7**	Ester **6**		**9**	**10**	**11**
+14.3°	+44.7°	(**9a**)	−55°	−88.3°	+127°
		(**9b**)	+4.2°		
−13.7°	−38.6°	(not measured)			−89.9°

The molecular formula ($C_{19}H_{26}O_5$) of (+)-keto diester **16** was established by elementary analysis and the mass spectrum (M$^+$ 334). In the proton NMR spectrum, it showed an intense singlet of *t*-butyl at 1.24 ppm, two sharp singlets of methoxycarbonyl group at 3.65 and 3.70 ppm, and 4H broad multiplet of aromatic proton signal centered at 7.2 ppm. All the signals for aliphatic protons, except *t*-butyl one, are very similar both in the shape and the chemical shifts to those of dimethyl 2-phenylethylsuccinate **17**. In the IR spectrum, it showed two carbonyl stretching bands at 1733 and 1689 cm^{-1}, in which the former was assigned to two ester-carbonyl groups and the latter to a keto-carbonyl bound to a phenyl group. A similarity of the NMR spectrum to that of **17** and the exsistence of a disubstituted benzene ring, in addition to a consideration of the structure of the starting material **15**, lead to the structure **16** for the keto diester. The UV spectrum of **16** showed no absorption maximum near 242 nm, the λ_{max} commonly observed in the alkyl phenyl ketones, but only shoulder of ε 2200 at 242 nm. This means that the conjugation between carbonyl and phenyl groups is hindered by a bulky *t*-butyl group (dihedral angle between carbonyl sp^2 and aromatic ring planes is calculated to be 65°).[9] Because the effect of carbonyl function on the ORD curves is believed to be small when the function is located far apart from the optically active center,[10] it would be possible to determine the absolute configuration of dimethyl 2-(*o*-pivaloylphenyl)ethylsuccinate (**16**) by comparing its ORD curve with that of optically active dimethyl 2-phenylethylsuccinate (**17**) of known configuration. In general, it has been shown that L-series of the alkyl or aralkylsuccinic acid show the minus Cotton effect or minus plain curves as follows.[11]



Scheme 3.

Compound	$[M]_{MeOH}$	Observed at	Type
(L)-(−)-Phenylsuccinic acid	−15450°	231 nm	minimum
(L)-(−)-Benzylsuccinic	−5260°	227 nm	minimum
(L)-(−)-2-Phenylethylsuccinic (**17**)	−4180°	222 nm	end absp.
(L)-(−)-3-Phenylpropylsuccinic	−2550°	221 nm	end absp.

The negative rotation of the ORD curve of (−)-**16** supports the (*S*)-configuration. The result shows that (−)-**11** gave (+)-**15**, which was transformed into (*S*)-(−)-**16** by oxidation.

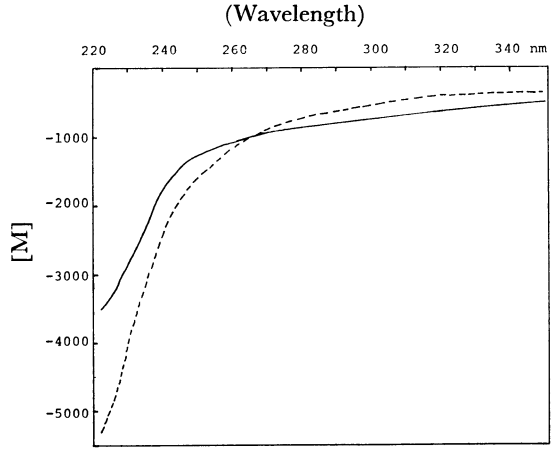


Fig. 2. ORD curves of the oxidation product **16**, $[\alpha]_D$= −15.4° (solid line) and an authentic **17**, $[\alpha]_D$ −39.7° (dotted line), dissolved in methanol.

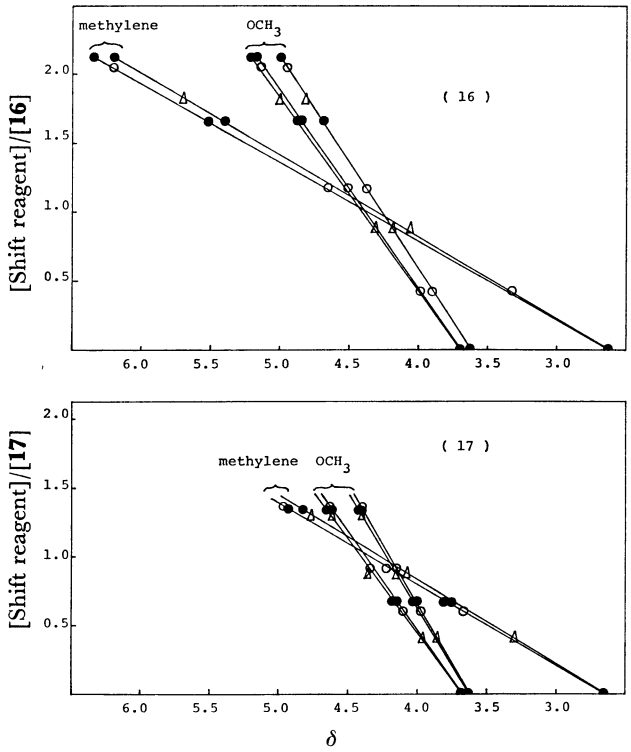


Fig. 3. Chemical shift changes of two methoxyl proton signals and one of methylene proton signal caused by the addition of a chiral shift reagent for compounds **16** and **17**.
△: (*S*)-(−)-Series, ○: (*R*)-(+)-series, ●: (±)-series.

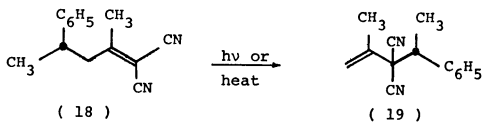
In order to obtain information about the relationship between absolute configurations and the NMR signal shifts caused by a chiral shift reagent,[12] we compared the NMR spectra between the optically active dimethyl 2-phenylethylsuccinates with and without substituent on the phenyl group.

We found that there is a regularity on the shift caused by *tris*-[3-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutylidene)-*d*-camphorato]europium(III), *i.e.*, the methoxyl-proton signal of lower field of the two methoxyl-proton signals of *S*-(−)-series shifted to the lower field more profoundly than those of *R*-(+)-series, but the signals assigned to one of methylene-protons adjacent to methoxycarbonyl group in the *S*-(−)-series shifted to a lesser extent than those in the *R*-(+)-series (Fig. 3).

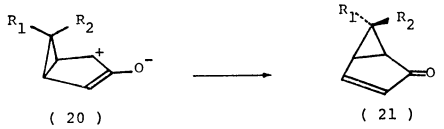
From the above results, the two series of correlations among the optically active products of the above transformations were established: *S*-(−)-**16**→*S*-(+)-**15**→*R*-(−)-**11**→(1*S*)-(−)-**6**→(1*S*)-(−)-**7**; *R*-(+)-**16**→*R*-(−)-**15**→*S*-(+)-**11**→(1*R*)-(+)-**6**→(1*R*)-(+)-**7**. Based on these experimental results, we can conclude that the photo-induced rearrangement of **6** to **11** must have proceeded with inversion of the configuration at C-1 in agreement with the prediction of the Woodward-Hoffmann rule.[13,14]

Discussion

The photochemical 1,3-sigmatropic rearrangement of **18** was established to proceed with retention of the configuration at the migrating carbon atom.[15,16] The thermal and photochemical rearrangements including cyclopropane ring are complicated because of the accompanying opening-reclosure process of three membered ring.[17–20] The thermal 1,4-shift in bicyclo-[3.1.0]hexenyl cation (**20**) is a rare example in which such an *exo-endo* isomerization does not accompanied by, and was found to proceed *via* slither motion with inversion of the configuration at C-6.[21]



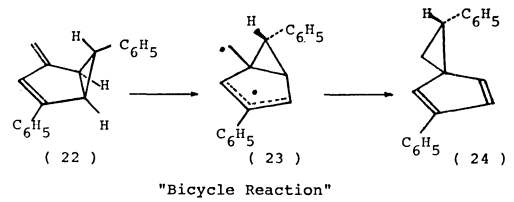
Scheme 4.



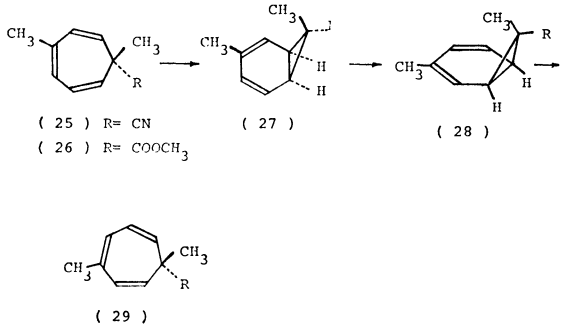
Scheme 5.

Furthermore, Zimmerman established that 4-methylene-2,6-*exo*-diphenylbicyclo[3.1.0]hept-2-ene(**22**) undergoes photoinduced skeletal rearrangement in a manner of slither motion with inversion of the configuration of the shifting carbon center, for which he proposed to rename "bicycle reaction."[22,23]

The Berson-Willcott rearrangement of cycloheptatrienes is thought to proceed *via* interconversion among its norcaradiene valence tautomers.[24] The stereochemi-



Scheme 6.



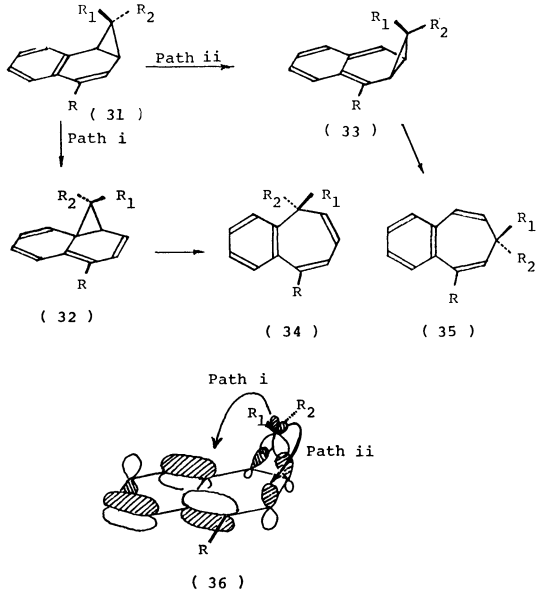
Scheme 7.

cal course of the benzophenone sensitized photochemical rearrangements of **25** and **26** had been studied by Klärner who found that the rearrangement is highly stereoselective (**25** 92% and **26** 76%) and proceeds with inversion at the migrating carbon C-7 similarly to the corresponding thermal rearrangement.[25-28] He proposed a stereoselective diradical process of the triplet states to account for the observed partial racemization.[29] These results are in line with the stereochemical course for path i of our previous results on the direct irradiation of 1a,7b-dihydro-1*H*-cyclopropa[*a*]-naphthalene derivative **1**. The rearrangement *via* path i was highly stereoselective as to configuration at C-1, even when an *exo-endo* mixture, after thermal equilibration of the methyl ester **1** obtained from optically active acid **30**, was used for the photolysis: That is, the product **4** (R_2=CH_2COOCH_3(*exo*)) retained the optical activity in high degree.

Furthermore, we found earlier that, when the *exo* and *endo* isomers of isopropyl derivative **5** were independently photolysed, they gave, without mutual interconversion, the same products each in so different rates as to support a mechanism of "bicycle reaction."[22]

From the above mentioned results, it is unlikely to assume a different stereochemical course for the *endo* isomer from that for the *exo* one. If the *exo*-**1** rearranges into *exo*-**4** *via* a course leading to an inversion at the migrating center and the *endo*-**1** does into *exo*-**4** *via* a course leading to a retention at the migrating center owing to some stereochemical reasons of the reaction, and *vice versa*, the optically active *exo-endo* mixture of **1** would give *exo*-**4** with considerable racemization. But this was not the case.

In the present case, the photochemical isomerization of optically active *exo*-1-ester **6** (optical purity>95%) to *endo*-1-ester was not observed during the reaction and the product **11** *via* path ii after photolysis retained its optical activity in high degree (>95%). For these reasons, we can conclude that the Berson-Willcott rearrangement of 1-methoxycarbonylmethyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes by direct irradiation, in general, takes place by way of 1,5-shift to both directions in a manner of "bicycle reactions," as shown in Scheme 8, in line with the prediction of the Woodward-Hoffmann rule [*Cf.* (**36**)].[6,14]



Scheme 8.

Experimental

The NMR spectra were taken on a JEOL Model PS-100 spectrometer with carbon tetrachloride as the solvent and TMS as the internal standard, unless otherwise specified. The chemical shifts are expressed in ppm from TMS. The IR spectra were recorded on a JASCO spectrometer Model IRE and the UV on a Hitachi Recording Spectrometer Model 323 with 95% ethanol as the solvent. GLC analysis was carried out on a Varian Aerograph Model 90P gas chromatograph under quoted conditions. The light source for photolysis, used throughout the experiments, was a Ushio High Pressure Mercury Lamp, UM-452, with Pyrex filter. The polarimeter used was a Rex Photoelectric one, type NEP-2, and the CD/ORD curves were recorded on a JASCO J-20 Automatic Recording Spectropolarimeter.

*3-t-Butyl-1a,7b-dihydro-1*H*-cyclopropa*[a]*naphthalene-1-carboxylic Acid* (*7*). To a melt of 1-*t*-butylnaphthalene (**8**) (37 g, 0.201 mol) containing 200 mg of copper powder, maintained at 145—150 °C, was added dropwise ethyl diazoacetate (5.14 g, 0.045 mol) over a period of 70 min with vigorous stirring. The mixture was further stirred at 145 °C for 1 h, and then 33.4 g of **8** was recovered by distillation under reduced pressure. The experiment was repeated six times with use of recovered **8**, and the collected residue in CH_2Cl_2 was filtered from copper powder and subsequently distilled to give 23 g of a mixture of three isomeric mono-esters, bp 120—143 °C (0.035 mmHg), contained 50% of ethyl ester of **7**. The oily product (11.8 g, 43.7 mmol) dissolved in 1 M 85% aq ethanolic KOH (130 ml) was refluxed for 20 h. The resulting solution was then diluted with water (130 ml) and reduced to a half volume under reduced pressure. After being washed with ether, the ice-cooled aq solution was acidified carefully with cold 2 M HCl in the presence of ether (100 ml) with stirring. The separated aq solution was extracted three times with ether. Usual work-up[6] of the combined ether solution gave **7** as

colorless crystals (3.31 g: 24% from **8**), mp 199—200 °C. IR ν_{max} (Nujol): 2670, 2580, 1690, 1321, 1214, 965, 897, 879, 771 cm^{-1}. NMR ($CDCl_3$): δ=0.75 (1H, dd, J=3.5, 3.5 Hz, H_1), 1.35 (9H, s), 2.72 (1H, m, H_{1a}), 3.16 (1H, dd, J=3.5 8.5 Hz, H_{7b}), 6.27 (1H, d, J=5.5 Hz), 7.0—7.9 (4H, m, Ar-H). Found: C, 79.37; H, 7.48%. Calcd for $C_{16}H_{18}O_2$: C, 79.37; H, 7.49%.

Optical Resolution of the Carboxylic Acid 7. A solution of freshly crystallized brucine (8.12 g, 18.8 mmol) and the carboxylic acid **7** (4.06 g, 16.8 mmol) dissolved in 50% aq methanol was allowed to stand for 36 d in a refrigerator, when crystals of the brucine salt have developed. Repeated fractional crystallization of the salt from aq methanol gave colorless prisms (1.06 g), mp 108—111 °C, $[\alpha]_D^{26}$ −44° (c= 1.1, $CHCl_3$). Extraction of this salt dissolved in $CHCl_3$ with 2 M aq NaOH, acidification of the extracts, and extraction with ether followed by recrystallization of the residue, gave colorless amorphous powder (580 mg), $[\alpha]_D^{27}$ −13.7° (c=1.0, $CHCl_3$). Similar treatment of the brucine salt obtained from the filtrate of recrystallization gave the (+)-acid; $[\alpha]_D^{19}$ +14.3° (c=1.1, $CHCl_3$), mp 84.5—86 °C as a colorless amorphous solid. The IR spectra of these optically active acids were identical with those of the racemic acid except for the absorptions at 965 and 879 cm^{-1}, which the active forms lacked. The optical purity of the (+)-acid was estimated to be more than 95% by comparison of the NMR spectrum of its methyl ester with that of the racemic one, using a chiral shift reagent, tris[3-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutylidene)-*d*-camphorato]Eu(III), as shown in Fig. 1.

The Absolute Configuration of (+)-Acid 7. Ozone generated from an ozonizer was passed through the carboxylic acid **7** suspended in 75% aq acetic acid (20 ml) for 3 h at room temperature. After addition of 10% aq H_2O_2 (12 ml), the resulting solution was kept at room temperature overnight and subsequently concentrated to dryness. The residue was then dissolved in 5% aq sodium hydrogen carbonate and washed with ether. The acidic fraction obtained from acidified aq solution was then treated with ethereal diazomethane. The GLC separation of the products gave three main peaks; (1) **14**, (4 mg; retention time (r.t.), 2 min); (2) **13** (10 mg; r.t. 10 min); (3) **12** (6 mg; r.t. 14 min). The compound **13** showed an identical NMR spectrum with that of a sample obtained from permanganate-oxidation and subsequent esterification of **30**. **12** NMR δ: 1.25 (9H, s), 2.2—3.1 (3H, m), 3.48 (3H, s), 3.67 (3H, s), 7.17 (4H, bs). IR ν_{max} (liq. film): 1688, 1725 cm^{-1}. Dimethyl *c*-3-[*o*-(methoxycarbonyl)phenyl]-*r*-1,*t*-2-cyclopropanedicarboxylate **13** NMR δ: 2.60 (2H, AB part of ABX), 3.37 (1H, X part of ABX), 3.44 (3H, s), 3.76 (3H, s), 3.89 (3H, s), 7.2—8.0 (4H, m). IR ν_{max} (liq. film): 1723, 1600, 1440, 1308, 1260, 1200, 1175, 1090, 1028, 908, 756 cm^{-1}. Found: C, 62.06; H, 5.67%. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52%.

Similar experiment with the (+)-acid **7**, $[\alpha]_D$ +11.7° (c= 1.2, $CHCl_3$), gave the triester **13**, $[\alpha]_D$ −55.8°, which had been previously related to the (+)-acid **30**, $[\alpha]_D$ +150°, of known stereochemistry (1*R*-(+)).[4]

rac- *and (+)-3-t-Butyl-1a,7b-dihydro-1-exo-methoxycarbonylmethyl-1H-cyclopropa[a]naphthalene (6).* To a stirred and cooled solution of racemic acid **7** (1.45 g, 6.0 mmol), dissolved in anhydrous benzene (120 ml), was added oxalyl dichloride (3.05 g, 24 mmol) at below 15 °C. After stirring the solution for 4.5 h at 6—10 °C, it was evaporated below 20 °C and the residue was evaporated with benzene (three times each 15 ml), under reduced pressure to give the acid chloride (**37**) as a yellow liquid [IR $\nu_{c=o}$: 1760 cm^{-1}]. To a dried ether solution (20 ml) of diazomethane, prepared from *N*-nitroso-*N*-methylurea (6.08 g), was added dropwise **37** dissolved in benzene (10 ml) over a period of 15 min with cooling (ice-water). After further stirring for 14 h at room temperature, the white floatings were filtered off, and the filtrate was concentrated to dryness to give the diazo ketone **38** as a yellow liquid (2.01 g) which solidified soon. The diazo ketone **38**, dissolved in methanol (2.01 g/650 ml) was divided into two portions. Each portion was independently irradiated under nitrogen atmosphere with an HPL for 16 min with external cooling (ice). The solutions were combined and subsequent evaporation of the solvent left an orange liquid (1.82 g), which was chromatographed on silica gel (70 g) with hexane–ether (93 : 3 v/v) as the solvent to give a pale yellow liquid (**6**) (1.02 g; 61% yield). IR ν_{max} (liq. film): 2956, 1736, 1489 1440, 1372, 1251, 1197, 1176, 766, 758 cm^{-1}. NMR δ: 0.22 (1H, m, H_1), 1.36 (9H, s), 1.84 (1H, m, H_{1a}), 2.24 (1H, dd, J=4, 8 Hz, H_{7b}), 3.68 (3H, s), 6.24 (1H, d, J=6 Hz), 7.0—7.8 (4H, m).

For elementary analysis, **6** (173 mg, 0.64 mmol) was hydrolyzed with 1 M 85% aq ethanolic KOH (10 ml) by refluxing for 2 h. The crystalline acid **39** (74 mg, 47%), was obtained by usual work-up and subsequent recrystallization from aq ethanol, mp 154.5—155.5 °C. IR ν_{max} (Nujol): 1700 cm^{-1}. Found: C, 79.61; H, 7.77%. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86%.

The same experiment was carried out with the optically active acid **7** (442 mg, 1.83 mmol), $[\alpha]_D$ +14.3°, to give the ester **6** (233 mg; 43%), $[\alpha]_D^{24}$ +44.7° (c=1.03, $CHCl_3$). IR ν_{max} (liq. film): 2956, 1736, 1489, 1440, 1372, 1251, 1197, 1176, 766, 758 cm^{-1}. The spectral data (IR, UV, and NMR) were identical with those of racemic ester **6**.

Photolysis of 3-t-Butyl-1a,7b-dihydro-1-exo-methoxycarbonylmethyl-1H-cyclopropa[a]napthalene (6). The methyl ester **6** (250 mg), dissolved in methanol (300 ml), was irradiated with an HPL through a Pyrex filter for 1 h under nitrogen atmosphere. After evaporation of the solvent, the residue was separated with use of GLC (10% Apiezone L on Chromosorb WAW, column temperature 203 °C): (1) **8** (r.t. 7 min), (2) *exo*- and *endo*-2a,7b-dihydrocyclobut[*a*]indenes **9** (r.t. **9a**, 13.6 min, **9b**, 16 min), (3) methyl 5-*t*-butyl-7*H*-benzocyclohepten-7-acetate (**11**) (r.t. 17 min), (4) methyl 9-*t*-butyl-5*H*-benzocycloheptene-5-acetate (**10**) (r.t. 21 min). The structures of these compounds were assigned based on the spectral data by comparing with those of the corresponding isopropyl derivatives.[6,30] **9a**: NMR δ: 1.08 (9H, s), 2.1—2.74 (2H, m), 2.98 (1H, bd, J= 1.5 Hz), 3.28 (1H, bddd, J=10, 5.5, 1.5 Hz), 3.68 (3H, s), 6.10 (1H, dd, J=2.7, 1.0 Hz), 6.38 (1H, d, J=2.7 Hz), 7.0—7.5 (4H, m). **9b**: NMR δ: 1.03 (9H, s), 2.2—2.8 (2H, m), 3.4—3.7 (2H, m), 3.68 (3H, s), 5.98 (1H, d, J=2.8 Hz), 6.48 (1H, d, J=2.8 Hz), 6.9—7.4 (4H, m) [contaminated with a small amount of aromatic impurities]. **10**: UV λ_{max} (EtOH): 262; λ_{min}: 243 nm. NMR δ: 1.36 (9H, s), 2.8—3.0 (3H, b), 3.62 (3H, s), 5.44 (1H, dd, H_6), 5.96 (1H, dd, H_7), 6.66 (1H, bd, H_8), 7.0—7.1 (3H, m), 7.5—7.66 (1H, m) [double irradiation: $J_{5,6}$=5 Hz, $J_{6,7}$=10 Hz, $J_{7,8}$=5 Hz; contaminated with a small amount of impurities]. **11**: UV λ_{max} (EtOH): 227, 247 (infl.) nm. NMR δ: 1.16 (9H, s), 2.24 (1H, m), 2.54 (2H, bd, J=7.5 Hz), 3.62 (3H, s), 5.75 (1H, d, J=10 Hz), 5.93 (1H, dd, J=10, 5 Hz), 6.48 (1H, dd, J=10, 1.8 Hz), 7.03—7.35 (3H, m), 7.6—7.8 (1H, m). Mass spectrum: *m/e* (%); 270 (40(M^+)), 255 (61), 214 (60), 197 (55), 181 (74), 171 (100), 141 (50), 57 (79). Found: C, 79.96; H, 8.26%. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%. Mp 51.5—52 °C.

The similar photolysis of the (+)-ester **6** (365 mg/430 ml; 16 min) gave **9** (50 mg, 14%), **11** (72 mg, 20%; $[\alpha]_D^{18.5}$ +127° (c=1.0, $CHCl_3$)), **10** (117 mg, 32%) in addition to **8** (41 mg). The optical purity of (+)-**11** was estimated to be more than 95% by applying the chiral shift reagent to its

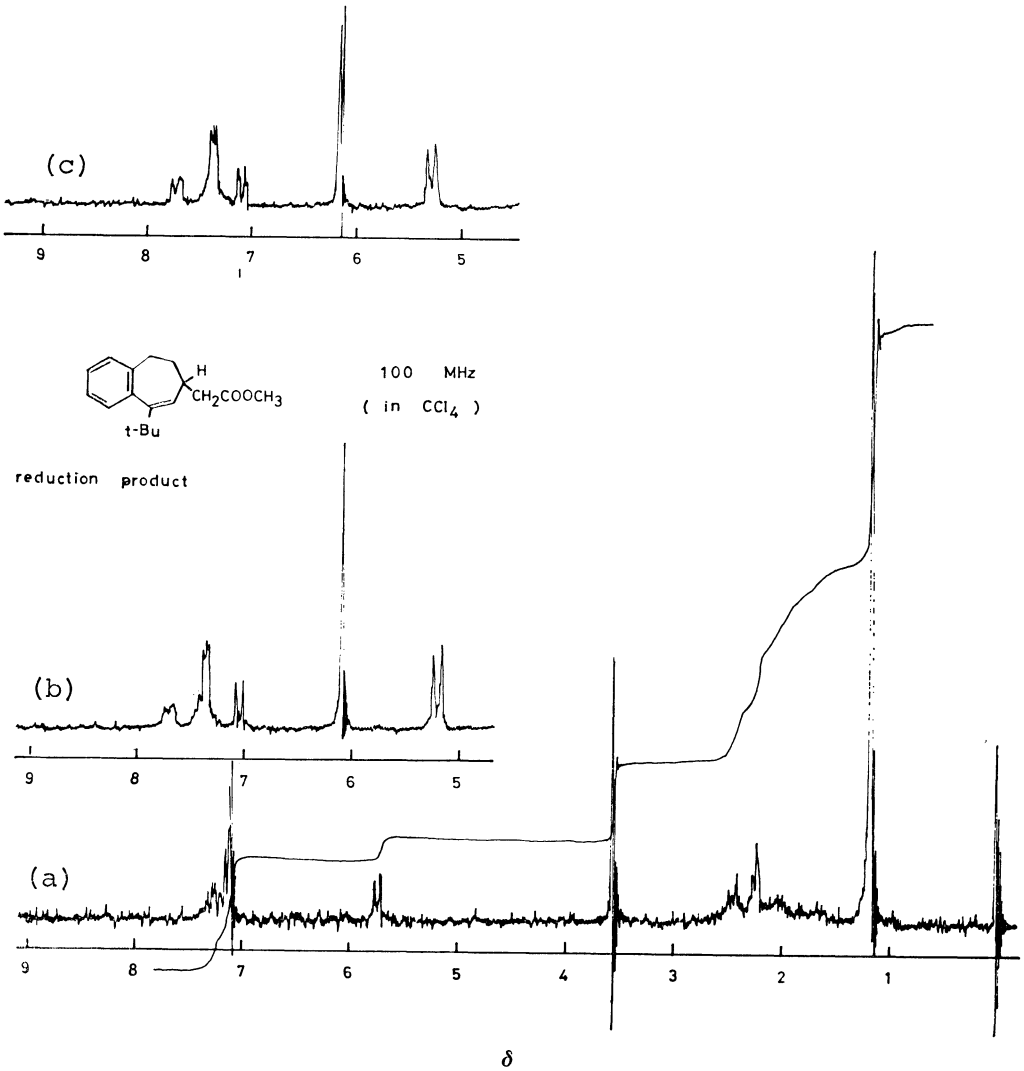


Fig. 4. ^1H NMR spectra of the hydrogenation product **15**.
(a) Original spectrum of optically active **15**, $[\alpha]_D = -61.2°$, (b) after addition of a chiral shift reagent to the above, (c) after addition of a chiral shift reagent to the racemic ester **15**.

dihydro derivative **15** similarly as mentioned above.

Hydrogenation of the 7H-Benzocycloheptene ***11***. The 7*H*-benzocycloheptene **11** (70 mg, 0.26 mmol), dissolved in ethyl acetate (10 ml), was hydrogenated over 10% Pd–C (20 mg) for 3.3 h until one molar equivalent of hydrogen was absorbed. Filtration from the catalyst and subsequent evaporation of the solvent left a yellow liquid (72 mg), which was revealed by NMR to contain **11**, 8,9-dihydro derivative of **11** (**15**), and tetrahydro derivative of **11** in a ratio of 13 : 80 : 7. The dihydro derivative **15** was separated by GLC (10% Apiezone L on Chromosorb WAW, column temperature 205 °C; r.t. 10 min). **15**: $[\alpha]_D$ −61.2° (c=1.0, $CHCl_3$). IR ν_{max} (liq. film): 2960, 1740, 1367, 1175, 1156, 849, 791, 760 cm^{-1}. UV λ_{max} (EtOH): 237 (log ε 3.90) nm, λ_{min} 225 (3.81). NMR δ: 7.25 (1H, m), 7.08 (3H, m), 5.73 (1H, d, J=6 Hz), 3.56 (3H, s), 2.76—1.60 (7H, m), 1.20 (9H, s). Mass spectrum: *m/e* (%); 272 (1.5 (M^+)), 215 (3), 183 (3), 155 (19), 141 (26.6), 128 (13.6), 115 (15.1), 57 (100), 41 (67.2). Found: C, 79.35; H, 8.94%. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88%.

Permanganate Oxidation of Methyl 5-t-Butyl-8,9-dihydro-7H-benzocycloheptene-7-acetate ***15***. To a stirred solution of perhydrodibenzo-18-crown-6 (156 mg, 0.42 mmol) in benzene (8 ml) was added potassium permanganate (66 mg, 0.42 mmol). After stirring for 1 h, **15** was added to the purple benzene solution and stirring was continued further for 2 d, until the purple color had beed discharged. Filration from the precipitates, and concentration of the filtrate gave a residue which was taken in benzene and chromatographed on silica gel to give 69% recovery of the starting material. Collected precipitates from repeated oxidation of the recovered ester **15** were combined with the initial precipitates and then extracted with hot water. The aqueous extracts were washed once with ether, acidified with 6 M hydrochloric acid, and extracted with ether to give colorless crystals (47 mg), which were esterified with ethereal diazomethane. Purification by TLC method (silica gel; ether–hexane=1 : 1) gave dimethyl (+)-2-[*o*-(2,2-dimethylpropanoyl)phenyl]ethylsuccinate **16**, $[\alpha]_D^{13.5}$ +16.0° (c=1.28, $CHCl_3$). **16** NMR δ: 7.2 (4H, m), 3.70 (3H, s), 3.65 (3H, s), 2.2—2.9 (5H, m), 1.6—2.0 (2H, m), 1.24 (9H, s). IR ν_{max} (liq. film): 2960, 1733, 1689, 1443, 1170, 969, 763 cm^{-1}. UV λ_{max} (EtOH): 233 (log ε 3.42), 251 (3.08), 271 nm (2.75). Mass spectrum: *m/e* (%); 334 (1.7 (M^+)), 303 (4.2), 277 (56.7), 245 (62.5), 217 (14.7), 185 (100), 57 (38). Found: C, 68.13; H, 7.85%. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84%.

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30) The fact that **10** is converted cleanly into a mixture of **9a** and **9b** (7 : 5) under the irradiation conditions supports the assignments. The photochemistry of **10** will be reported in due time together with photo-induced reaction of other 5*H*-benzocycloheptene derivatives.