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THE ABSOLUTE CONFIGURATION OF *cis*-2-PHENYLCYCLOPROPANE-CARBOXYLIC ACID AND RELATED COMPOUNDS

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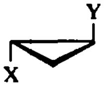
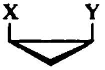
Abstract— Decarboxylation of (+)-*cis*-2-phenylcyclopropane-carboxylic acid (**3b**) with lead tetraacetate in benzene or in the presence of iodine gives (−)-(1*R*:2*R*)-*trans*-1,2-diphenylcyclopropane (**7**) and (−)-(1*R*:2*S*)-*trans*-2-phenylcyclopropyl iodide (**12a**), respectively. This establishes the absolute configuration of (+)-**3b** as 1*S*:2*R*. Asymmetrically synthesized (−)-(*R*)-2-phenylmethylenecyclopropane (**24**) and (−)-(*R*)-phenylspiropentane (**25**) are correlated with (+)-**3b** through (+)-(1*S*:2*R*)-*cis*-1-methyl-2-phenylcyclopropane (**27**), whose ozonolysis affords (−)-(1*R*:2*S*)-*cis*-2-methylcyclopropane-carboxylic acid (**28**). Finally it has been found that (1*S*:2*S*)-*trans*-2-phenylcyclopropyllithium (**14**) adds to benzyne intermediate stereospecifically to produce (1*S*:2*S*)-*trans*-1-(*o*-lithiophenyl)-2-phenylcyclopropane (**15**).

Cyclopropane derivatives are chiral when they have two substituents X and Y at 1, 2 positions. The absolute configuration of *trans* isomer **1** has been established as shown.[1–4] In this paper we wish to report the absolute configuration of *cis* isomers **2** and those of 2-phenyl-methylenecyclopropane (**24**) and phenylspiropentane (**25**), which can be correlated with the *cis* isomer **2b**.



1

(+)-**1a**: X = Y = Me[1]
(+)-**1b**: X = Y = Ph[2]
(+)-**1c**: X = Y = COOH[3]
(+)-**1d**: X = Ph, Y = COOH[3]
(+)-**1e**: X = Ph, Y = Me[4]
(+)-**1f**: X = COOH, Y = Me[4]



2

(+)-**2a**: X = Ph, Y = COOH
(+)-**2b**: X = Ph, Y = Me
(−)-**2c**: X = COOH, Y = Me

The absolute configuration of cis-*2-phenylcyclopropanecarboxylic acid**

Decarboxylation of alkanecarboxylic acids with lead tetraacetate gives rise to alkyl radicals.[6] We have subjected cyclopropanecarboxylic acids to this reaction to investigate the behaviour of resulting cyclopropyl radicals. Each of *trans*- and *cis*-2-phenylcyclopropanecarboxylic acid (**3a** and **3b**) was decarboxylated with lead tetraacetate in benzene at 80° in the presence of a catalytic amount of cupric acetate and pyridine. From the reaction mixture the same products **7**–**11** (R = H) were identified in every case. Product distribution was shown in Table 1.

All these products are explained by assuming the intermediacy of cyclopropyl radical **4**, which attacks the solvent benzene to give **7** and abstracts hydrogen to afford **8**. Simple isomerization of **4** gives allyl radical **5**, which must be an intermediate for **9**.

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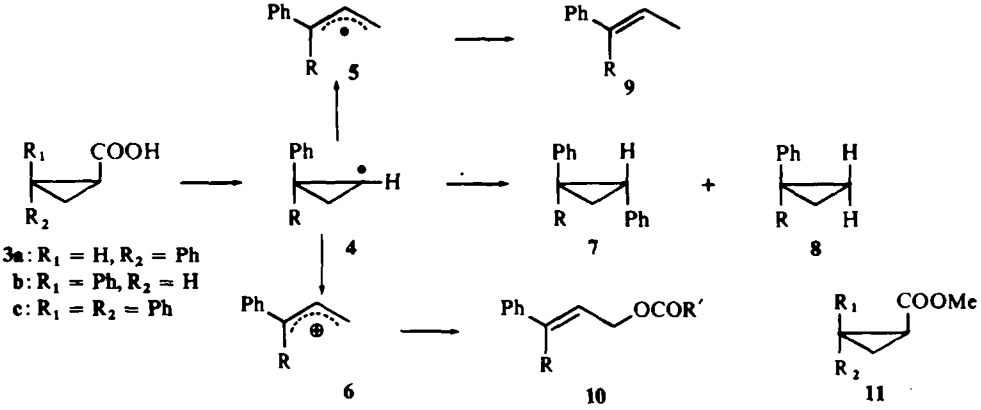
* This paragraph was partly published in a preliminary form. See Ref. 5.

Oxidation of **4** by metal ions such as Pb^{III}, Pb^{IV} and/or Cu^{II} followed by ring opening furnishes allyl cation **6**,[7] which constitutes a precursor of S_N products **10**. The origin of methyl group in **11** would probably be ascribed to decarboxylation of acetic acid present in the reaction media.[*] Similar results were obtained for 2,2-diphenylcyclopropanecarboxylic acid (**3c**) (Table 1).



R = H for **3a**, **b**; R = Ph for **3c**.

TABLE 1. DECARBOXYLATION OF CYCLOPROPANECARBOXYLIC ACIDS WITH LEAD TETRAACETATE

Acid	Reaction time, hr	Conversion, %	Product, %[a] 7	8	9	10		11
3a	4	52	15	1	3	3[b]		35
3b	2	75	43	1	1	7[b]		17
3c	22·5	47	3	2	1	40[c]	38[d]	13

[a] Yields were estimated on GLC.

[b] *trans*-Cinnamyl acetate.

[c] 3,3-Diphenylallyl acetate.

[d] 3,3-Diphenylallyl 2,2-diphenylcyclopropanecarboxylate.

Notably both **3a** and **3b** gave only *trans* isomer of 1,2-diphenylcyclopropane **7**.[†] This stereoselectivity in the phenylative decarboxylation must be explained on the basis of planar or rapidly inverting configuration of cyclopropyl radical carbon.[9] Evidence was obtained in support of the retention of configuration at the phenyl-substituted carbon of *trans*-acid **3a**, as (+)-(1*S*:2*S*)-**3a**, $[\alpha]_D^{20}$ +376° (99% optical purity),[3] gave (+)-(1*S*:2*S*)-**7**, $[\alpha]_D^{20}$ +418°.[2][‡] These results suggest that attack of benzene on the common intermediate, 2-phenylcyclopropyl radical **4**, occurs exclusively from the site opposite to the originally existing phenyl group. The participation of phenyl group as seen in phenonium ions should have minor role in the radical **4** if any. Laevorotatory isomer (1*R*:2*R*) of **7**, $[\alpha]_D^{20}$ −266°, was obtained upon

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[*] In the reaction of cinnamic acid with lead tetraacetate, the formation of methyl cinnamate was observed. For the reaction of arylcyclopropanes with lead tetraacetate *in acetic acid*, see Ref. 8.

[†] Homogeneity of **7** was established on GLC and NMR.

[‡] All the rotations in this paper were measured in chloroform solutions. The highest specific rotation of **7** recorded previously is 117° (neat). See Ref. 2*a*.

similar treatment of partially resolved *cis*-acid (+)-**3b**, $[\alpha]_D^{20}$ +20°. Assuming the retention of configuration at the phenyl-substituted carbon of **3b**, we may conclude that (+)-**3b** should have the absolute configuration of 1*S*:2*R*. Such a conclusion was warranted by the following halogenative decarboxylation, whose data are also included in Table 2.

Barton's iododecarboxylation involves the treatment of alkanecarboxylic acids with lead tetraacetate and iodine, and this reaction too is considered to proceed *via* alkyl radicals.[10] Each isomer of **3a** and **3b** was treated with lead tetraacetate in the presence of iodine under irradiation to afford only the *trans* isomer of 2-phenylcyclopropyl iodide (**12a**) in 43 and 42% yield, respectively.* Dextrotatory *trans*-acid (+)-(1*S*)-**3a**, $[\alpha]_D^{20}$ + 360° (95% optical purity), gave (+)-(1*S*:2*R*)-**12a**, $[\alpha]_D^{20}$ + 188°, whose absolute configuration was determined as follows. The same iodide (+)-**12a** was subjected to halogen-lithium interchange by means of n-butyllithium[11], the resulting product was carbonated and then esterified with diazomethane to give back

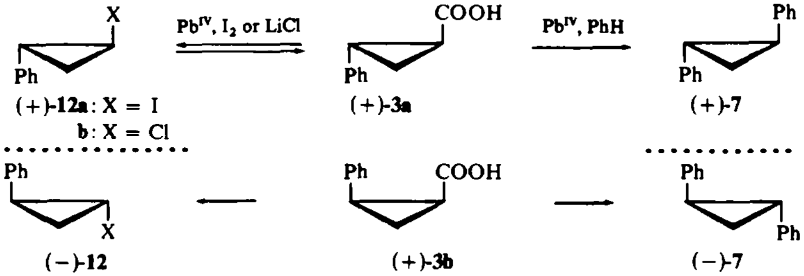


TABLE 2. CHEMICAL TRANSFORMATIONS OF OPTICALLY ACTIVE ACIDS

Acid	$[\alpha]_D^{20}$, deg.	c,[a] g/100 ml	Optical[b] purity, %	Product[c]	$[\alpha]_D^{20}$, deg.	c,[a] g/100 ml	Yield, %
(+)-**3a**	+376	0·88	99	(+)-**7**	+418	0·96	18
(+)-**3b**	+20	1·40		(−)-**7**	−266	1·94	22
(+)-**3a**	+360	1·00	95	(+)-**12a**	+188	0·80	43
(+)-**3a**	+308	2·34	81	(+)-**12a**	+149	2·00	41
(−)-**3b**	−16	1·00		(+)-**12a**	+128	2·06	42
(+)-**3a**	+376	0·88	99	(+)-**12b**	+145	2·34	23
(+)-**3b**	+20	1·40		(−)-**12b**	−100	0·44	20

[a] All rotations were measured in chloroform solutions with a cell of 5 cm length.

[b] Based on the highest value 381°, ref. 3.

[c] The chemical purity of products was checked by TLC, GLC, NMR and elemental analyses.

the methyl ester of (+)-(1*S*:2*S*)-**3a**, $[\alpha]_D^{20}$ +270° (*c* 1·22) or 81% optical purity. Thus the stereochemistry of this Barton reaction is quite similar as the phenylation reaction and the retention of configuration at the phenyl-substituted carbon of **3a** is calculated to be 86%. Furthermore the Barton reaction of 2,2-diphenylcyclopropanecarboxylic acid (**3c**) gave only 2,2-diphenylcyclopropyl iodide (**13a**) in a 57% yield.* These observations exclude the possibility of phenyl migration in this kind of radical reactions.[12] Now that iododecarboxylation of *cis*-acid (+)-**3b**, $[\alpha]_D^{20}$ +16°, gave

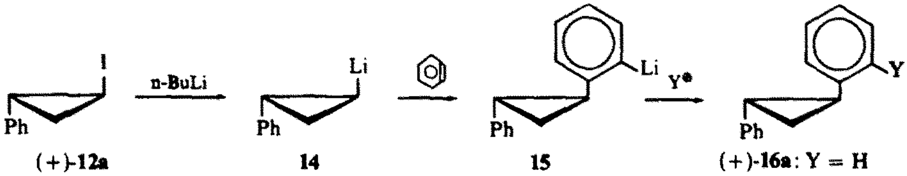
* Homogeneity of **12a** and **13a** was established on GLC and NMR.

(−)-(1R:2S)-**12a**, $[\alpha]_D^{20}$ −128°, the absolute configuration of (+)-**3b** was reconfirmed to be 1S:2R.

Table 2 contains furthermore similar results obtained in Kochi's chlorodecarboxylation of **3a** and **3b**, which was effected by means of lead tetraacetate and lithium chloride.[13] These three pairs of data in Table 2 (phenylative decarboxylation, iodo- and chlorodecarboxylation) permit us to calculate the specific rotation of optically pure *cis*-acid **3b** as ca. 30° in chloroform.

Synthesis of dissymmetric trans-1-(o-*lithiophenyl*)-2-*phenylcyclopropane**

Configurational stability of cyclopropyllithium has been firmly established.[11] Based on this, we have correlated *trans*-iodide (+)-**12a** with *trans*-acid (+)-**3a** through (1S:2S)-*trans*-2-phenylcyclopropyllithium (**14**), and the absolute rotation of **12a** was calculated to be 220° in chloroform *vide supra*. Next we examined the stereospecific addition of cyclopropyllithium **14** to benzyne intermediate generated *in situ* to produce (1S:2S)-*trans*-1-(*o*-lithiophenyl)-2-phenylcyclopropane (**15**). Dissymmetric lithio compound **15** would serve as a versatile intermediate for the syntheses of some new *o*-substituted *trans*-1,2-diphenylcyclopropane (**16**) of known optical purity. The stereospecific phenylation of vinyllithium with benzyne has recently been reported.[15]



(+)-**12a** **14** **15** (+)-**16a**: Y = H
b: Y = COOMe

The mixture of *trans*-iodide (+)-**12a**, $[\alpha]_D^{20}$ +149° (*c* 2·00) or 68% optical purity, and *o*-bromofluorobenzene in ether was treated with n-butyllithium in hexane at −40° and warmed to −10° to allow decomposition of *o*-fluorophenyllithium to benzyne. The resulting organolithium was quenched with methanol to give the desired product (+)-(1S:2S)-*trans*-1,2-diphenylcyclopropane (**16a** ≡ **7**), $[\alpha]_D^{20}$ +361° (*c* 1·32), in a 20% yield. Carbonation of similarly prepared (1S:2S)-**15** followed by diazomethane treatment gave (+)-(1S:2S)-*trans*-1-(*o*-methoxycarbonylphenyl)-2-phenylcyclopropane (**16b**), $[\alpha]_D^{20}$ +127° (*c* 0·86), in a 19% yield. As none of *cis* isomer of **16a** and **16b** was detected in these reactions, thus stereospecifically synthesized **16a** and **16b** should have the rotation of 530° and 190° in chloroform, respectively, if optically pure **12a** was employed. Based on this value, the optical yield is estimated to be 80% in the phenylative decarboxylation of (+)-**3a** to (+)-**7** ≡ **16a**.

The absolute configuration of phenylspiropentane and related compounds

Asymmetric carbenoid reactions have been achieved on the decomposition of some diazo compounds by means of *soluble, dissymmetric* copper chelate such as bis[N-(R- and S-)-α-phenethylsalicyladiminato]copper(II), (R)- and (S)-**17**.[16] For example, thermolysis of ethyl diazoacetate in the presence of styrene and (S)-17 gave (−)-(1R:2R)-ethyl *trans*-2-phenylcyclopropanecarboxylate (**19**) and (−)-(1R:2S)-ethyl *cis*-2-phenylcyclopropanecarboxylate (**20**) in a 6 and 10% optical yield, respectively.

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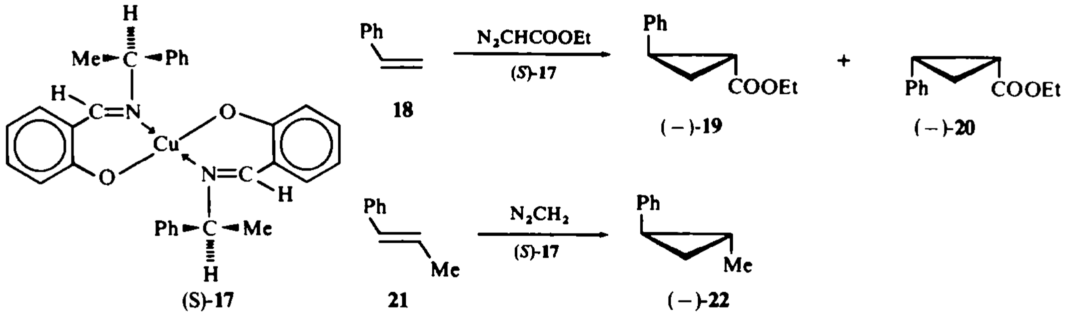
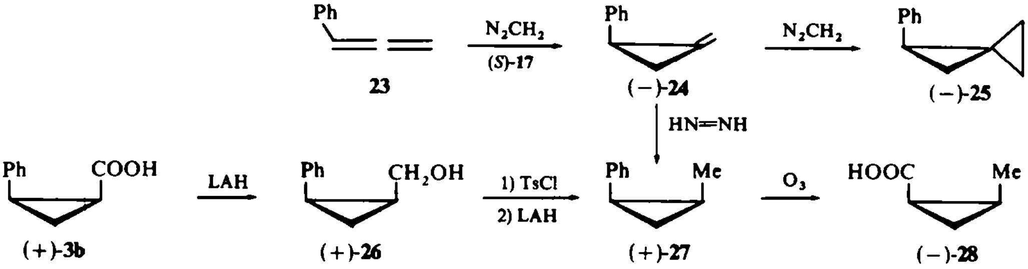
* For the syntheses of dissymmetric lithioferrocenes, see Ref. 14.

Diazomethane itself was decomposed in the presence of *trans*-propenylbenzene to yield (−)-(1*R*:2*R*)-*trans*-1-methyl-2-phenylcyclopropane (**22**) of 8% optical purity.



Further asymmetric induction was observed on decomposition of diazomethane in the presence of phenylallene (**23**) and (*S*)-**17** to produce (−)-2-phenylmethylenecyclopropane (**24**) and (−)-phenylspiropentane (**25**).[17] Since asymmetric synthesis of spiropentane **25** was attained at the stage of precursory methylenecyclopropane **24** formation, they should have the same absolute configuration and optical purity. Diimide reduction of **24** is known to give *cis*-1-methyl-2-phenylcyclopropane (**27**), instead of *trans* isomer **22**, as the result of preferential attack of diimide from the sterically less hindered site of double bond. We now treated a mixture of (−)-**24**, $[\alpha]_D^{20}$ $-35°$* and (−)-**25**, $[\alpha]_D^{20}$ $-55°$ (*c* 3·54), with potassium azodicarboxylate and acetic acid to afford (+)-**27**, $[\alpha]_D^{20}$ $+7·7°$ (*c* 4·56). Based on this, the absolute configuration of (−)-**24** and (−)-**25** was determined as *R* and the optical yield in the asymmetric synthesis is estimated to be 12%, for the same *cis*-hydrocarbon (+)-**27** of the known configuration was prepared as follows.



(+)-(1*S*:2*R*)-Methyl *cis*-2-phenylcyclopropanecarboxylate, $[\alpha]_D^{20}$ $+27°$ (*c* 2·04), obtained from *cis*-acid (+)-**3b**, $[\alpha]_D^{20}$ $+15°$ (*c* 2·00) or 50% optical purity, was subjected to LAH reduction to give (+)-(1*S*:2*R*)-*cis*-1-hydroxymethyl-2-phenylcyclopropane (**26**), $[\alpha]_D^{20}$ $+39°$ (*c* 2·42). Tosylate of this alcohol was reduced again with LAH to yield *cis*-hydrocarbon (+)-(1*S*:2*R*)-**27**, $[\alpha]_D^{20}$ $+32°$ (*c* 2·08). Moreover ozonolysis of (+)-**27**, $[\alpha]_D^{20}$ $+7·7°$ (*c* 4·56), gave (−)-(1*R*:2*S*)-*cis*-2-methylcyclopropanecarboxylic acid (**28**), $[\alpha]_D^{20}$ $-8°$ (*c* 0·80). As the same assignment for **28** was attained recently,[18a] our original one (1*S*:2*R*) for (+)-**3b** was again substantiated.

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* Facile thermal racemization of **24** was noted. See Ref. 17. The corresponding enantiomers were obtained in the use of (*R*)-**17**. See Experimental.

Finally these chemically established results were compared with those deduced from physical methods. Brewster's calculation[19] was applied to some cyclopropane derivatives. The calculated and found values are summarized in Table 3. While every sign of rotation was correctly predicted, the agreement in magnitude was not so satisfactory.

TABLE 3. CALCULATION OF CONFORMATIONAL ASYMMETRY ACCORDING TO BREWSTER

Compound Absolute configuration	**7** (1*S*:2*S*)	**12a** (1*S*:2*R*)	**12b** (1*S*:2*R*)	**24** (*R*)	**25** (*R*)
$[M]_D$ (calcd)	+327	+583	+397	−327	−140
$[M]_D$ (found)[a]	+1030	+540	+230	−380	−660
$[\alpha]_D$ (found)[a]	+530	+220	+150	−290	−460

[a] Taken in chloroform solutions at 20°.

This calculation method can not be applied to *cis*-1,2-disubstituted cyclopropanes (e.g. **3b**, **26**, **27** and **28**), in which case we resorted to another method. Recent advances in ORD and CD studies revealed that aromatic chromophores attached to asymmetric carbon atom are dissymmetrically perturbed.[20] Verbit *et al.* investigated the UV and CD spectra of phenyl-substituted *trans*-cyclopropanes (**3a** and **22**) to find out the following fact. Disubstituted cyclopropanes with a phenyl ring attached to a carbon of *R* configuration are characterized by the negative sign of Cotton effect at ^1L_b (250–275 nm) and ^1L_a (215–225 nm) transitions.[20b] The CD spectrum (in methanol) of the *trans* isomer (+)-(1*S*:2*S*)-**7**, $[\alpha]_D^{20}$ +418° (*c* 0·96), consisted of two parts: one at 260–280 nm with $[\theta]$ $+2{\cdot}5 \times 10^4$ and the other one at 230 nm with $[\theta]$ $+7{\cdot}5 \times 10^4$. In contrast, however, the *cis* isomer (−)-(1*R*:2*S*)-**3b** and (+)-(1*S*:2*R*)-**26** did not show any detectable peak of CD under our experimental conditions.*

EXPERIMENTAL

All b.ps and m.ps are uncorrected. Microanalyses were performed at the Elemental Analyses Centre of Kyôto University. IR spectra were obtained in neat liquid film on a Shimadzu IR-27-G spectrophotometer. NMR spectra were taken in 10% CCl_4 solns on a JEOL C-60-H spectrometer and chemical shifts are reported in δ values relative to TMS as an internal standard. NMR signals in singlet are designated as s, doublet as d, triplet as t and multiplet as m. GLC analyses and separations were performed with columns packed with HVSG (30%) and Apiezon L (30%) on Celite 545 or SE 30 (7%) on Chromosorb. Optical rotations were measured in $CHCl_3$ solns with a cell of 5 cm length. UV and CD spectra were run on a JASCO ORD/UV/CD-5 spectropolarimeter. All reactions were carried out under N_2 atmosphere and controlled by TLC (Silica Gel G).

Decarboxylation of cyclopropanecarboxylic acids

Decarboxylation of trans-*2-phenylcyclopropanecarboxylic acid* (**3a**). In a 500 ml flask were placed **3a** (5·0 g, 31 mmoles), $Pb(OAc)_4$ (33 g, 74·5 mmoles), $Cu(OAc)_2 \cdot H_2O$ (0·5 g), pyridine (0·2 g) and benzene (200 ml). The stirred mixture was heated under reflux for 4 hr to evolve 1700 ml of CO_2 gas. After the reaction mixture was treated with water and filtered, the filtrate was shaken with 10% KOH aq to recover the unchanged **3a** (2·4 g, 48%) upon acidification. Benzene soln was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. Residual oil was shown by GLC to consist of five components, two of which were identified without isolation to be *trans*-propenylbenzene (3%) and phenylcyclopropane (1%), respectively, by comparison of

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* Very recently the ORD and CD of *cis*- and *trans*-2-methyl-3-phenyloxirane were reported by I. Moretti and G. Torre, *Tetrahedron Letters* 2717 (1969).

their retention times with those of authentic samples (2 columns). Following products were isolated by means of column chromatography (silica gel-benzene) and identified by comparison of their spectra (IR and NMR) with authentic ones: *trans*-1,2-diphenylcyclopropane[21] (15%, b.p. 140°/3·5 mm), *trans*-cinnamyl acetate (3%) and methyl *trans*-2-phenylcyclopropanecarboxylate (35%, b.p. 100°/3 mm). Any trace of *cis*-1,2-diphenylcyclopropane[21] could not be detected (GLC and NMR).

Decarboxylation of cis-2-*phenylcyclopropanecarboxylic acid* (**3b**). A mixture of **3b** (1·0 g, 6 mmoles), $Pb(OAc)_4$ (4·0 g, 8·5 mmoles), $Cu(OAc)_2 \cdot H_2O$ (0·15 g) and pyridine (0·2 g) in benzene (35 ml) was heated for 2 hr at reflux. Work-up gave the recovered **3b** (0·25 g, 25%) and a colourless oil (0·50 g), which was shown by GLC to consist of five components: *trans*-propenylbenzene (1%), phenylcyclopropane (1%), *trans*-1,2-diphenylcyclopropane (43%), *trans*-cinnamyl acetate (7%) and methyl *cis*-2-phenylcyclopropanecarboxylate (17%, b.p. 83°/4 mm). Any trace of *cis*-1,2-diphenylcyclopropane was not detected (GLC).

Decarboxylation of 2,2-diphenylcyclopropanecarboxylic acid (**3c**). A mixture of **3c** (4·75 g, 20 mmoles), $Pb(OAc)_4$ (9·0 g, 20 mmoles), $Cu(OAc)_2 \cdot H_2O$ (0·4 g) and pyridine (0·2 g) in benzene (100 ml) was heated for 22·5 hr as above. Work-up gave the recovered **3c** (2·5 g, 53%) and a neutral oil, which consisted of six components. Two of them were identified without isolation to be 1,1-diphenyl-1-propene[22] (1%) and 1,1-diphenylcyclopropane[23] (2%), respectively. Distillation of the crude oil gave a fraction (1·32 g), b.p. 120–129°/0·1 mm, from which two products were isolated by means of column chromatography (silica gel-benzene) and their structures were determined on the basis of spectral data. *Methyl 2,2-diphenylcyclopropanecarboxylate* (13%), b.p. 120°/0·06 mm, IR: 3055, 3030, 2925, 1745, 1600, 1495, 1438, 1380, 1270, 1192, 1170, 1095, 1080, 1060, 1020, 750 and 700 cm^{-1}, NMR: δ 1·43 (m, 1H), 2·03 (m, 1H), 2·42 (m, 1H), 3·30 (s, 3H) and 7·05 (m, 10H). (Found: C, 81·0; H, 6·3. $C_{17}H_{16}O_2$ requires: C, 80·9; H, 6·4%). 3,3-*Diphenylallyl acetate* (40%), b.p. 140°/0·06 mm, IR: 3060, 3030, 2925, 1740, 1600, 1495, 1448, 1380, 1363, 1075, 1025, 955, 770, 760 and 700 cm^{-1}, NMR: δ 2·00 (s, 3H), 4·56 (d, 2H), 6·12 (t, 1H) and 7·17 (m, 10H). (Found: C, 81·2; H, 6·2. $C_{17}H_{16}O_2$ requires: C, 80·9; H, 6·4%).

Two compounds were isolated from the distillation residue by column chromatography (silica gel-benzene): 1,1,2-triphenylcyclopropane[24] (3%), IR: 3080, 3030, 1980–1660, 1600, 1500, 1445, 1070, 1030, 760 and 696 cm^{-1}, NMR: δ 1·85 (m, 2H), 2·77 (m, 1H), 6·97 and 7·11 (m, 15H), and 3,3-*diphenylallyl 2,2-diphenylcyclopropanecarboxylate* (38%), m.p. 95–97°, IR: 3080, 3030, 2950, 1980–1660, 1740, 1605, 1495, 1445, 1388, 1365, 1270, 1160, 990, 940, 760 and 700 cm^{-1}, NMR: δ 1·43 (m, 2H), 2·12 (m, 1H), 2·50 (m, 1H), 4·40 (d, 2H), 5·79 (t, 1H) and 7·12 (m, 10H). (Found: C, 86·4; H, 6·3. $C_{31}H_{26}O_2$ requires: C, 86·5; H, 6·1%).

(+)-trans-1,2-*Diphenylcyclopropane* (7) *from* trans-*acid* (+)-**3a**. Acid **3a** was resolved by fractional recrystallization of quinine salts from $MeOH–H_2O$ (3:1).[3] A mixture of (+)-**3a** $[\alpha]_D^{20}$ +376° (*c* 0·884), 2·5 g (15 mmoles), $Pb(OAc)_4$ (10 g, 23 mmoles), $Cu(OAc)_2 \cdot H_2O$ (0·1 g) and pyridine (0·2 g) in benzene (100 ml) was heated under reflux for 15 hr. Work-up gave the recovered **3a** (0·97 g, 39%) and a neutral oil (1·3 g), which was separated on a silica gel column (hexane) to give 0·33 g (18%) of (+)-7, b.p. 134–135°/3·5 mm, $[\alpha]_D^{20}$ +418° (*c* 0·956). IR spectrum and GLC retention time were identical with those of authentic one. (Found: C, 92·6; H, 7·4. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%).

(−)-trans-1,2-*Diphenylcyclopropane* (7) *from* cis-*acid* (+)-**3b**. Acid **3b** was resolved by fractional recrystallization of quinine salts from $MeOH–H_2O$ (3:1).[25] A mixture of (+)-**3b**, ($[\alpha]_D^{20}$ +20° (*c* 1·40), 1·2 g, 7·4 mmoles), $Pb(OAc)_4$ (3·3 g, 7·4 mmoles), $Cu(OAc)_2 \cdot H_2O$ (0·05 g) and pyridine (0·1 g) in benzene (60 ml) was heated at reflux for 2 hr. Work-up afforded the recovered **3b** (0·51 g, 42%) and a neutral oil, which was separated by column chromatography (silica gel-hexane) to give 0·18 g (22%) of (−)-7, b.p. 135°/3 mm, $[\alpha]_D^{20}$ −266° (*c* 1·94). IR spectrum and GLC retention time were identical with those of the sample obtained from (+)-**3a**. (Found: C, 92·8; H, 7·2. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%).

Iododecarboxylation of cyclopropanecarboxylic acids

(+)-trans-2-*Phenylcyclopropyl iodide* (**12a**) *from* trans-*acid* (+)-**3a**. To a stirred mixture of (+)-**3a**, ($[\alpha]_D^{20}$ +360° (*c* 1·00), 3·0 g, 18·5 mmoles) and $Pb(OAc)_4$ (15 g, 34 mmoles) in benzene (100 ml) was added dropwise a benzene soln (170 ml) of iodine (4·5 g, 18 mmoles) at reflux temp under irradiation of tungsten lamp in the course of 2 hr. When CO_2 gas evolution ceased and the I_2 colour was no longer discharged, the reaction mixture was treated with water and filtered. The unchanged **3a** (1·6 g, 53%) was recovered and the neutral products were purified by means of chromatography (silica gel-hexane) to give (+)-**12a** (0·90 g, 43%), b.p. 77–78°/2 mm, $[\alpha]_D^{20}$ +188° (*c* 0·80), IR: 3080, 3050, 1980–1660, 1608, 1500, 1210, 1180, 1095, 1075, 1040, 1020, 970, 750 and 695 cm^{-1}, NMR: δ 1·40 (m, 2H), 2·35 (m, 2H) and 7·12 (m, 5H). The spectral data and GLC analyses indicated that this sample was free from the *cis* isomer of **12a**[8]. As this compound decomposed gradually, satisfactory analyses were not obtained.

(+)-trans-2-*Phenylcyclopropyl iodide* (**12a**) *from* cis-*acid* (−)-**3b**. To a mixture of (−)-**3b** ($[\alpha]_D^{20}$ −16° (*c* 1·00), 0·60 g, 3·7 mmoles) and $Pb(OAc)_4$ (3·1 g, 7·0 mmoles) in benzene (50 ml) was added a benzene soln (60 ml) of iodine (1·0 g, 4·0 mmoles) in 3 hr at reflux temp under irradiation by tungsten lamp. Work-up afforded the recovered **3b** (0·11 g, 18%) and a crude oil, which was chromatographed (silica gel-hexane) and distilled to give (+)-**12a** (0·31 g, 42%), $[\alpha]_D^{20}$ +128° (*c* 2·06). Spectral data and GLC retention time were identical with those of the sample obtained from (+)-**3a**.

2,2-*Diphenylcyclopropyl iodide* (**13a**). To a mixture of **3c** (1·6 g, 6·7 mmoles) and $Pb(OAc)_4$ (7·2 g, 16 mmoles) in benzene (70 ml) was added a benzene soln (100 ml) of iodine (2·0 g, 8·0 mmoles) in 1 hr under reflux and irradiation of tungsten lamp. Usual work-up gave the recovered **3c** (0·07 g, 4%) and a neutral oil (1·3 g), which was shown to be a single isomer by GLC (2 columns). A sample (0·2 g) was purified by short column chromatography (silica gel-hexane) followed by concentration *in vacuo* to give white crystals of **13a** (0·18 g, total yield 57%), m.p. 44–45·5°. The structure was established on the basis of spectral data: IR: 3090, 3060, 3030, 1980–1660, 1600, 1500, 1450, 1275, 1200, 1080, 1050, 1020, 900, 755 and 700 cm^{-1}, NMR: δ 1·79 (AB pattern in ABX, 2H), 3·33 (X pattern in ABX, 1H), 7·15 (s, 5H) and 7·27 (s, 5H). NMR data excluded possible contamination of this sample by 1,2-diphenylcyclopropyl iodide. Correct elemental analyses were not obtained owing to the instability of this compound.

Chemical correlation of trans-*iodide* (+)-**12a** *with* trans-*acid* (+)-**3a**

To a soln of (+)-**12a** ($[\alpha]_D^{20}$ +188° (*c* 0·80), 0·80 g, 3·3 mmoles) in ether (50 ml) was added a soln of n-butyllithium (0·9 M in hexane, 7 ml, 6·3 mmoles) in ether (100 ml). After stirring for 30 min at 15–20°, the mixture was cooled to −10° and dry CO_2 gas was bubbled into the mixture. Work-up followed by alkaline extraction gave crude (+)-**3a** (0·47 g). Esterification with diazomethane gave methyl ester of (+)-**3a** (0·27 g, 47%), b.p. 100°/3 mm, $[\alpha]_D^{20}$ +270° (*c* 1·22) or 81% optical purity based on 334°. IR spectrum and GLC retention time were identical with those of authentic one.[4] (Found: C, 75·4; H, 7·1. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·9%).

Chlorodecarboxylation of cyclopropanecarboxylic acids

(+)-trans-2-*Phenylcyclopropyl chloride* (**12b**) *from* trans-*acid* (+)-**3a**. A mixture of (+)-**3a** ($[\alpha]_D^{20}$ +376° (*c* 0·884), 1·6 g, 10 mmoles), $Pb(OAc)_4$ (4·5 g, 10 mmoles) and LiCl (0·42 g, 10 mmoles) in benzene (100 ml) was heated under reflux and stirred for 1·5 hr, when no more CO_2 gas was evolved. The reaction mixture was treated with water and filtered. The unchanged **3a** (0·75 g, 47%) was recovered by shaking the filtrate with 10% KOH aq followed by acidification. The neutral soln was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel-hexane) to give (+)-**12b** (0·18 g, 23%), b.p. 87–88°/14 mm, $[\alpha]_D^{20}$ +145° (*c* 2·34). IR and NMR spectra were superimposable with reported ones.[26] GLC analyses established the homogeneity of this sample.

(−)-trans-2-*Phenylcyclopropyl chloride* (**12b**) *from* cis-*acid* (+)-**3b**. A mixture of (+)-**3b** ($[\alpha]_D^{20}$ +20° (*c* 1·40), 0·78 g, 5·1 mmoles), $Pb(OAc)_4$ (2·3 g, 5·2 mmoles) and LiCl (0·23 g, 5·4 mmoles) in benzene (70 ml) was heated for 3 hr. Work-up afforded the recovered **3b** (0·43 g, 55%) and a neutral oil, which was purified on column chromatography (silica gel-hexane) to give (−)-**12b** (0·065 g, 20%), b.p. 99–100°/14 mm, $[\alpha]_D^{20}$ −100° (*c* 0·438). IR spectrum and GLC retention time were identical with those of the sample obtained from (+)-**3a**.

2,2-*Diphenylcyclopropyl chloride* (**13b**). A mixture of **3c** (4·0 g, 16·8 mmoles), $Pb(OAc)_4$ (7·3 g, 16·5 mmoles) and LiCl (0·7 g, 16·5 mmoles) in benzene (60 ml) was heated for 3 hr as above. Work-up gave the recovered **3c** (2·0 g, 50%) and a neutral oil, which was shown to be homogeneous on GLC. Purification by short column chromatography (silica gel-hexane) followed by concentration *in vacuo* gave a white crystalline mass of **13b** (0·26 g, 14%), m.p. 70–71·5° (lit.[26b] 71–72°), IR: 3060, 3035, 1980–1660, 1600, 1495, 1450, 1305, 1080, 1040, 1020, 930, 755 and 695 cm^{-1}, NMR: δ 1·65 (d, 2H), 3·58 (t, 1H) and 7·05–7·20 (m, 10H).

Reaction of trans-2-*phenylcyclopropyllithium* (**14**) *with benzyne intermediate and subsequent derivatizations*

(+)-trans-1,2-*Diphenylcyclopropane* (**16a** = **7**) *from* trans-*iodide* (+)-**12a**. To a soln of *trans*-iodide (+)-**12a** ($[\alpha]_D^{20}$ +149° (*c* 2·00), 1·3 g, 5·3 mmoles) and *o*-bromofluorobenzene (1·45 g, 8·6 mmoles) in ether (200 ml) was added a hexane soln of *n*-butyllithium (35 ml, 21 mmoles) in 30 min at −45° ~ −40°. After addition was completed, the mixture was warmed to −10° in the course of 3 hr with stirring. The reaction mixture was treated with MeOH and then with water. Work-up gave an oily concentrate, which was shown by GLC to consist of three components. The main products isolated on preparative GLC was (+)-**16a** (0·2 g, 20%), b.p. 125°/2 mm, $[\alpha]_D^{20}$ +361° (*c* 1·32). (Found: C, 92·7; H, 7·4. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%). Minor by-products were phenylcyclopropane and 2-fluorobiphenyl. Any trace of *cis* isomer of **16a** was not detected on GLC and NMR.

(+)-trans-1-(o-*Methoxycarbonylphenyl*)-*2-phenylcyclopropane* (**16b**) *from* trans-*iodide* (+)-**12a**. To a soln of (+)-**12a** ($[\alpha]_D^{20}$ +149° (*c* 2·00), 2·0 g, 8·2 mmoles) and *o*-bromofluorobenzene (2·2 g, 13 mmoles) in ether (200 ml) was added a hexane soln of n-butyllithium (48 ml, 32 mmoles) in a similar manner as above. After the mixture was warmed to −10° in the course of 3 hr, dry CO_2 gas was bubbled into the mixture. The reaction mixture was extracted with 5% KOH aq (100 ml) and the crude acid was esterified with diazomethane. Purification by preparative GLC gave a colourless oil of (+)-**16b** (0·4 g, 19%), b.p. 120°/0·03 mm, $[\alpha]_D^{20}$ +127° (*c* 0·86). The structure was established on the basis of spectral data: IR: 3080, 3045, 3010, 2960, 2860, 1730, 1600, 1595, 1485, 1450, 1435, 1285, 1260, 1208, 1125, 1085, 1050, 755, 730 and 710 cm^{-1}, NMR: δ 1·37 (m, 2H), 2·00 (m, 1H), 3·00 (m, 1H), 3·58 (s, 3H), 7·20 (m, 8H) and 7·80 (m, 1H). (Found: C, 80·7; H, 6·5. $C_{17}H_{16}O_2$ requires: C, 80·9; H, 6·4%). Minor by-products were methyl *trans*-2-phenylcyclopropanecarboxylate and 2-fluoro-2′-methoxycarbonylbiphenyl.

Diimide reduction of (+)-*2-phenylmethylenecyclopropane* (**24**) *to* (−)-cis-*1-methyl-2-phenylcyclopropane* (**27**)

The reaction of phenylallene (**23**) with diazomethane in the presence of Cu chelate, (*R*)-**17**, gave after distillation (40°/0·05 mm) a mixture of **23**, **24** and **25** in a ratio of 3:3:4 (GLC), $[\alpha]_D^{20}$ +32·5° (*c* 9·60).[17] To a soln of this mixture (12 g) and potassium azodicarboxylate (30 g) in MeOH (500 ml) was added AcOH (60 ml) dropwise in the course of 4 hr at room temp. The mixture was stirred for 12 hr and then treated with water. Distillation of the products *in vacuo* followed by GLC purification gave 0·39 g of (−)-**27**, b.p. 66°/12 mm, $[\alpha]_D^{20}$ −7·7° (*c* 4·56). (Found: C, 90·8; H, 9·3. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·2%). Phenylspiropentane (**25**) was also collected, b.p. 87–87·5°/12 mm, $[\alpha]_D^{20}$ +55° (*c* 3·54). (Found: C, 91·8; H, 8·5. Calc. for $C_{11}H_{12}$: C, 91·6; H, 8·4%). Their IR spectra were identical with those reported.[17] From these optical data we can calculate that original (+)-**24**, the precursor of (−)-**27**, should have the rotation of $[\alpha]_D^{20}$ +35°.

Lithium aluminium hydride reduction of (+)-cis-*2-phenylcyclopropanecarboxylic acid* (**3b**)

(+)-cis-1-*Hydroxymethyl-2-phenylcyclopropane* (**26**). To a soln of LAH (1·0 g, 29 mmoles) in ether (20 ml) was added in 20 min an etheral soln (20 ml) of methyl ester of (+)-**3b** (b.p. 83°/4 mm, $[\alpha]_D^{20}$ +27° (*c* 2·04), 0·80 g, 4·5 mmoles), which was prepared by diazomethane treatment of (+)-**3b**, $[\alpha]_D^{20}$ +15·0° (*c* 2·00). The mixture was stirred overnight at room temp and for an additional 1 hr at reflux temp. Work-up gave (+)-**26** (0·56 g, 83%), b.p. 84–86°/3 mm, $[\alpha]_D^{20}$ +39·2° (*c* 2·42), IR: 3250, 3050, 3000, 2920, 2870, 1600, 1500, 1450, 1300, 1240, 1135, 1080, 1020. 900. 840, 800, 760, 700 and 695 cm^{-1}. (Found: C, 81·0; H, 8·3. $C_{10}H_{12}O$ requires: C, 81·0; H, 8·2%)

(+)-cis-1-*Methyl-2-phenylcyclopropane* (**27**). To a soln of (+)-**26** ($[\alpha]_D^{20}$ +39·2°, 0·50 g, 3·4 mmoles) in 2,6-lutidine (0·7 ml) was added tosyl chloride (1·3 g, 6·8 mmoles) in 2,6-lutidine (0·8 ml) at 0°. After the mixture was stirred for 2 hr at 20°, the pasty product was poured into water and extracted with ether. Work-up gave a crude tosylate (1·40 g), which was immediately subjected to the reduction. A soln of tosylate (1·4 g) in ether (9 ml) was added to a soln of LAH (1·75 g, 45·5 mmoles) in ether (26 ml) at 0°. After addition of THF (4 ml) the mixture was stirred overnight at room temp. Work-up gave (+)-**27** (0·26 g, 58%), b.p. 70°/15 mm, $[\alpha]_D^{20}$ +32·2° (*c* 2·08). IR and NMR spectra was identical with those of the authentic one.[17] (Found: C, 90·8; H, 9·2. Calc. for $C_{10}H_{12}$: C, 90·8; H, 9·2%).

Ozonolysis of (−)-cis-*1-methyl-2-phenylcyclopropane* (**27**) to (+)-cis-*2-methylcyclopropanecarboxylic acid* (**28**)

A stream of crude ozone was passed through a soln of (−)-**27** ($[\alpha]_D^{20}$ −7·7° (*c* 4·56), 0·22 g, 1·7 mmoles) in CCl_4 (10 ml) at 40° for 4 hr. After the mixture was allowed to stand at room temp overnight with 30% H_2O_2 (3 ml), additional 1 ml of 30% H_2O_2 was added and the mixture was heated to gentle reflux for 1 hr. The reaction mixture was treated with dil NaOH aq and aq layer was washed with ether, acidified with conc HCl and extracted with ether. The etheral soln was washed with water, dried (Na_2SO_4) and concentrated *in vacuo* to give (+)-**28** (0·04 g, 24%), b.p. 95°/16 mm, $[\alpha]_D^{20}$ +8·0° (*c* 0·80). IR spectrum was identical in every respect with the reported one.[9a] (Found: C, 60·5; H, 8·2. Calc. for $C_5H_8O_2$: C, 60·0; H, 8·1%).

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