Reactivities of Stable Rotamers. XXXII. Chlorodecarboxylation of 3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoic Acid Rotamers[1,2]

Michinori ŌKI,* Yasushi TAGUCHI, Toshiyuki OKAMOTO, Tsutomu MIYASAKA, Koji HAMADA, Shinji TOYOTA, Katsumi YONEMOTO,† and Gaku YAMAMOTO†

Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700
†Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

(Received July 5, 1993)

Rotational isomers of the title carboxylic acid were treated with lead(IV) acetate in the presence of lithium chloride or benzyltriethylammonium chloride in benzene. The *ap*-isomer afforded a chloride, which was expected from normal chlorodecarboxylation, in addition to a cyclized compound, which was produced by radical addition to a near-by benzene ring. By contrast, the *sc*-isomer afforded no normal chloride, but a benzylic chloride, which was formed by hydrogen transfer to the radical site in the 9-substituent from the benzylic position, was the main product. In addition, an acetonyl ester of the original *sc*-carboxylic acid and a small amount each of 1-acetoxymethyl compound and an olefin were obtained. Possible mechanisms of formation of these compounds are discussed on the ground of the stability of the benzylic radical and participation of a methyl group.

When we compare reactivities of rotational isomers, the difference may largely depend on the active intermediate species which are produced during the reaction and interact with various substituents within the molecule or in other molecules. We have demonstrated that acylium-cationic species which are produced in vicinity of a methoxyl group and a methyl group behave quite differently in some cases,[3] whereas those which are produced in vicinity of halogens did not show significant differences from those apart from such substituents.[4] However, if a cationic species are produced from an amine by diazotization, a halogen substituent shows distinct stabilization effect[5] and a methyl group undergoes an insertion reaction.[6]

As an extension of such works, it will be interesting to see the reactivity of radicals which are produced in rotameric positions. Whereas there are various ways of generation of radicals, we chose a Hunsdiecker type reaction, oxidation of a carboxylic acid with lead(IV) acetate in the presence of chloride anion. This reaction is known to proceed via a chain reaction mechanism, which involves a coordination compound of lead(IV) with a radical.[7] The radical ligand is produced by oxidation of the carboxylate anion followed by decarboxylation.

Results

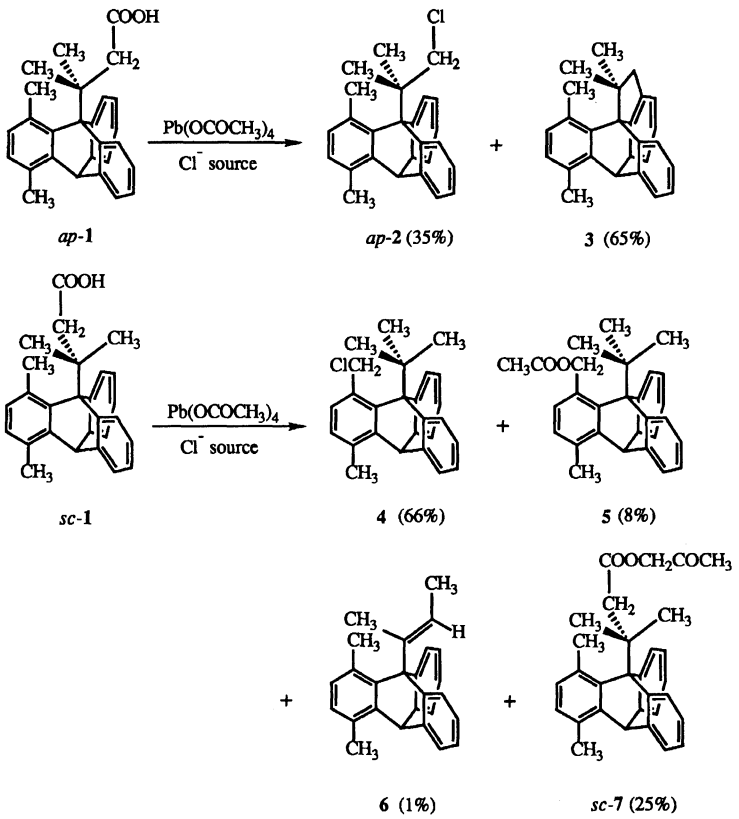
When the carboxylic acid rotamers (*ap*-**1** and *sc*-**1**) were individually treated with lead(IV) acetate in benzene and heated under reflux in the presence of lithium chloride, the products shown in Scheme 1 were obtained with the yields shown in the scheme as normalized values. The yields of the products are dependent on the kinds and the relative amounts of the chloride source. The dependence is shown in Tables 1 and 2.

It is clear from Table 1, that the use of 1 equivalent of lithium chloride as a chloride source gives a very poor yield of the chloride (*ap*-**2**) from *ap*-**1**. This is due to the poor solubility or the very low concentration of lithium chloride in benzene under the conditions. Increasing the amount of lithium chloride increases the production of the chloride. However, the cyclized product (**3**) is still a main product if lithium chloride is used for the reaction of *ap*-**1**.

The use of benzyltriethylammonium chloride increases the yield of the chloride (*ap*-**2**) considerably: The use of 10 equivalents of the chloride gives 90% yield of *ap*-**2** and the yield of **3** is diminished to 10%, although some benzyltriethylammonium chloride remained undissolved and benzyl 3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoate was formed to some extent.

In the case of *sc*-**1**, the yield of compound **4** is rather high even for lithium chloride as a chloride source. The yield of the acetate (**5**) decreases as the concentration of the chloride ion increases and it is not detected when 10 equivalents of benzyltriethylammonium chloride is used. As the chloride concentration in solution rises, the formation of the olefin (**6**) becomes undetected.

Identification of the products was carried out as follows. The *ap* chloride (*ap*-**2**) was an expected product, if the reaction proceeds normally, and was identified by consistent ^{1}H NMR spectra as well as elemental analyses. Preparation of compound **3** has been reported[8] and the product was identical with the authentic specimen. Benzyl *ap*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoate was prepared independently from the *ap*-acid and benzyl alcohol. Compound **5** was identified by ^{1}H NMR spectra, in which one aromatic methyl proton signal was missing from the starting material, a new signal ascribable to a methylene proton pair appeared, and the 9-substituent was a *t*-butyl. The elemental analysis was consistent with this structure. Compound **4** could be converted to compound **5** by treating it with silver tetrafluoroborate in acetic acid. Spectral data and elemental analysis were also consistent with this structure. Compound **6** was already reported[9] and was identical



Scheme 1. Reaction products of chlorodecarboxylation with 4 equivalents of LiCl.

Table 1. Effects of Excess of the Chloride Source on Product Distributions from *ap*-**2**

LiCl[a]/equiv	$C_6H_5CH_2N(C_2H_5)_3Cl$[b]/equiv	*ap*-**2**/%	**3**/%
1.0	—	12	88
4.0	—	35	65
—	1.0	71	29
—	4.0	82	18
—	10.0	90	10

a) A part of lithium chloride remained undissolved. b) A part of benzyltriethylammonium chloride remained undissolved when 10 equivalents were used.

Table 2. Effects of Excess of the Chloride Source on Product Distribution from *sc*-**2**

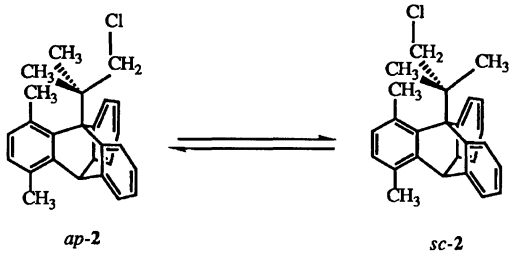
LiCl[a]/equiv	$C_6H_5CH_2N(C_2H_5)_3Cl$/equiv	**4**/%	**5**/%	**6**/%	*sc*-**7**/%
1.0	—	42	15	9	34
4.0	—	66	8	1	25
—	1.0	78	1	—	21
—	4.0	57	—	—	43

a) A part of lithium chloride remained undissolved.

with the authentic specimen.

Since *sc*-**2** seemed to be absent in the product mixture, this compound was independently prepared by isomerization of *ap*-**2**. The absence of *sc*-**2** in the product was confirmed by this process (Scheme 2).

Compound **7** posed a difficulty in structure determination. Its ^{1}H NMR spectra indicated that there were two pairs of geminal methylene protons, both of which were diastereotopic. Their chemical shift differences implied that one pair was close to the chiral axis and the other was remote from it. ^{13}C NMR spectra indicated that there were a ketone carbonyl and an ester group. IR spectra of the compound was also consistent with the ^{13}C spectra interpretation, though the two carbon-



Scheme 2. Isomerization of compound **2**.

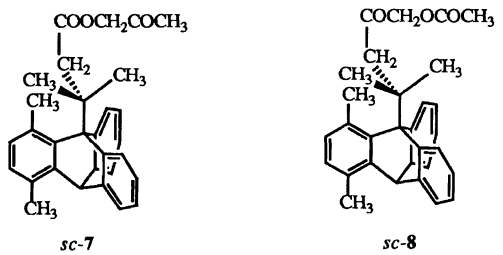
yls showed an overlapped absorption. From these spectral data, the possible structures of the unknown compound became two, *sc*-**7** and *sc*-**8**, but it was not possible to determine which was the correct structure from the spectra (Scheme 3). Thus the structure was proved by independent synthesis and X-ray crystallography.

The synthesis of the acetonyl ester (**7**) was straightforward, although heating time necessary for the *sc* isomer was very long. The carboxylic acid dissolved in tetrahydrofuran was treated with sodium hydride to convert it into sodium salt and then heated with chloroacetone to produce the desired acetonyl ester. This compound was found to be identical with the product mentioned above.

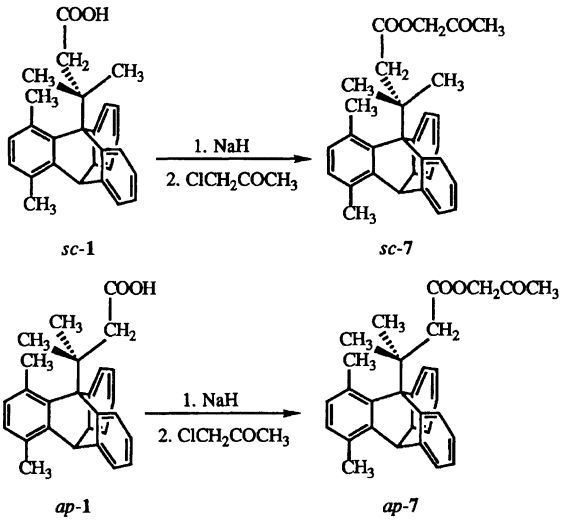
In order to confirm the absence of the *ap*-acetonyl ester (*ap*-**7**) from *ap*-**1**, the *ap*-form was also prepared. No signals ascribable to *ap*-**7** were found in the spectrum of the reaction mixture from *ap*-**1** (Scheme 4).

Results of X-ray crystallography agreed with the conclusion from chemical evidence. The ORTEP drawing of the compound is given in Fig. 1. Atomic coordinates are listed in Table 3. Selected values of bond lengths, bond angles, torsion angles, and dihedral angles made by three benzene rings are shown in Table 4.

The triptycene skeleton is very similar with other triptycenes with substituents whose structures have been published.[10—13] The methyl substituent at the 1-position of the skeleton is strongly bent away from the 9-substituent, as was the case for a similar compound.[14] The ester moiety takes an almost upright position relative to the triptycene skeleton, the structure being attributed to steric effects which make other conformations very unstable. Dihedral angles made by three benzene rings are almost the same, as is expected from almost the same effective bulkiness of the three groups



Scheme 3. Possible products in conformity with spectral data.



Scheme 4. Syntheses of acetonyl esters.

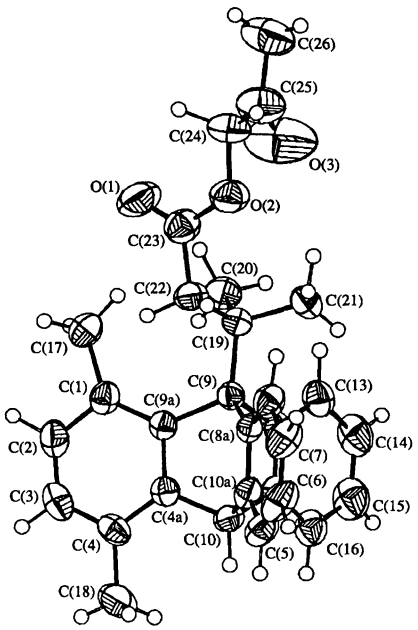


Fig. 1. ORTEP drawing of acetonyl *sc*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoate (*sc*-**7**) with thermal ellipsoids with 50% probabilities.

which are attached to the carbon atom that is connected to the 9-position.

Discussion

The results of the work on the concentration effects of the chloride source in solution clearly indicate that the lead(IV) complex formation is not necessarily complete under the reaction conditions. For the *ap*-form, increasing the amount of lithium chloride increases the yield of *ap*-**2** at the expense of **3**. For the *sc*-isomer, formations of **5** and **6** decrease on increasing the chloride source. These may evidence that oxidation of the formed radicals and formation of the chloride (**4**) are competing in the case of *sc* and chloride formation is

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in Acetonyl *sc*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate[a)]

Atom	x	y	z	B_{eq}[b)]
O(1)	0.4294(1)	0.0256(2)	1.2981(2)	7.41(9)
O(2)	0.3192(1)	−0.0204(1)	1.4130(2)	5.21(6)
O(3)	0.3780(2)	−0.1712(2)	1.3735(3)	11.7(1)
C(1)	0.3535(2)	0.1106(2)	0.8211(3)	3.62(8)
C(2)	0.3765(2)	0.1685(2)	0.7097(4)	4.48(9)
C(3)	0.3250(2)	0.1988(2)	0.5970(4)	4.7(1)
C(4)	0.2452(2)	0.1715(2)	0.5852(3)	3.72(8)
C(4a)	0.2208(2)	0.1140(2)	0.6919(3)	3.02(7)
C(5)	0.0267(2)	0.1408(2)	0.8508(4)	4.3(1)
C(6)	−0.0029(2)	0.1519(2)	0.9956(5)	5.2(1)
C(7)	0.0371(2)	0.1191(2)	1.1210(4)	5.0(1)
C(8)	0.1095(2)	0.0755(2)	1.1046(3)	3.96(9)
C(8a)	0.1425(1)	0.0646(1)	0.9606(3)	2.98(7)
C(9)	0.2225(1)	0.0177(2)	0.9159(3)	2.90(7)
C(9a)	0.2713(1)	0.0826(1)	0.8139(3)	2.91(7)
C(10)	0.1356(2)	0.0795(2)	0.6827(3)	3.36(8)
C(10a)	0.0985(2)	0.0969(2)	0.8353(3)	3.31(7)
C(11)	0.1452(2)	−0.0122(2)	0.6718(3)	3.33(7)
C(12)	0.1909(2)	−0.0464(2)	0.7938(3)	3.21(8)
C(13)	0.2024(2)	−0.1318(2)	0.7920(3)	4.25(9)
C(14)	0.1702(2)	−0.1782(2)	0.6690(4)	5.4(1)
C(15)	0.1265(2)	−0.1416(2)	0.5492(4)	5.6(1)
C(16)	0.1130(2)	−0.0584(2)	0.5500(3)	4.37(9)
C(17)	0.4255(2)	0.0881(2)	0.9264(4)	5.6(1)
C(18)	0.1888(2)	0.2062(2)	0.4608(4)	5.4(1)
C(19)	0.2691(2)	−0.0228(2)	1.0581(3)	3.40(8)
C(20)	0.3435(2)	−0.0740(2)	1.0061(4)	4.46(9)
C(21)	0.2121(2)	−0.0835(2)	1.1429(4)	4.6(1)
C(22)	0.2958(2)	0.0463(2)	1.1742(3)	3.95(9)
C(23)	0.3566(2)	0.0168(2)	1.2971(3)	4.6(1)
C(24)	0.3705(2)	−0.0557(2)	1.5334(4)	5.1(1)
C(25)	0.3958(2)	−0.1405(2)	1.4952(4)	6.4(1)
C(26)	0.4436(3)	−0.1856(3)	1.6182(5)	8.3(2)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/Å^2=(8\pi^{2/3})\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

favored when the chloride concentration is high. These make a sharp contrast to the cases where excess of the chloride source drastically decreases the yield of the corresponding chloride, reported in the literature.[15,16)] The cause for this discrepancy must be the steric effects of the compound in question, which disfavor the formation as well as retard the rates of formation of the complex involving the chloride ion.

The results with *ap*-**1** are normal but there may be an argument whether the cyclized compound (**3**) was formed via a radical or a cation. For the following reasons, we wish to attribute the formation of **3** to radical cyclization. Firstly, if a cation intervenes, we should have observed formation of olefins that are derived from the cation. The rates of Wagner–Meerwein rearrangement should be fast[17,18)] and addition of the cation to the benzene ring in proximity and the rearrangement must be competing processes, as found in diazotization of amines.[6)] Secondly, the oxidation of the intervening radical to the corresponding cation is known to be rather slow, if lead(IV) acetate is the only oxidizing reagent, although copper(II) ion easily oxidizes the radicals.[7)] Thirdly if the chloride source is present in excess, as is seen in Table 1, the yield of compound **3** diminishes and that of **2** increases. Addition of radicals to benzene is known to be rather fast,[19)] and the highly proximal location between the produced radical and the benzene rings should facilitate the addition.

Formation of **4** from *sc*-**1** must be attributed to facile hydrogen transfer from the 1-methyl group to the radical center (**9**) which is produced in the substituent at the 9-position. This is reasonable because the benzylic radical (**10**) which is newly formed must be more stable than **9** and the distance between the 1-methyl group and the radical center in **9** is very short, the C–C distance being only 3.03 Å. The only product which originates from the originally formed radicals is compound **6**, of which formation decreases as the chloride source concentration increases (Scheme 5). This will mean that, though the radical **9** has a certain lifetime that is long enough for oxidation under the conditions, it is very short because of the facile hydrogen transfer from the 1-methyl. The formation of detectable amount of the olefin **6** might imply presence of some participation of the 1-methyl group in stabilization of the radical **9** but the details are not known. If the cation **10** is formed, other olefins could be also formed. But as are known, other olefins are much less stable than compound **6**, preventing detection by the NMR method.[9)] We wish to attribute absence of any *sc*-chloride to the steric effects of the 1-methyl and other groups in the *sc*-position, which make the coordination of the radical to lead very unstable.

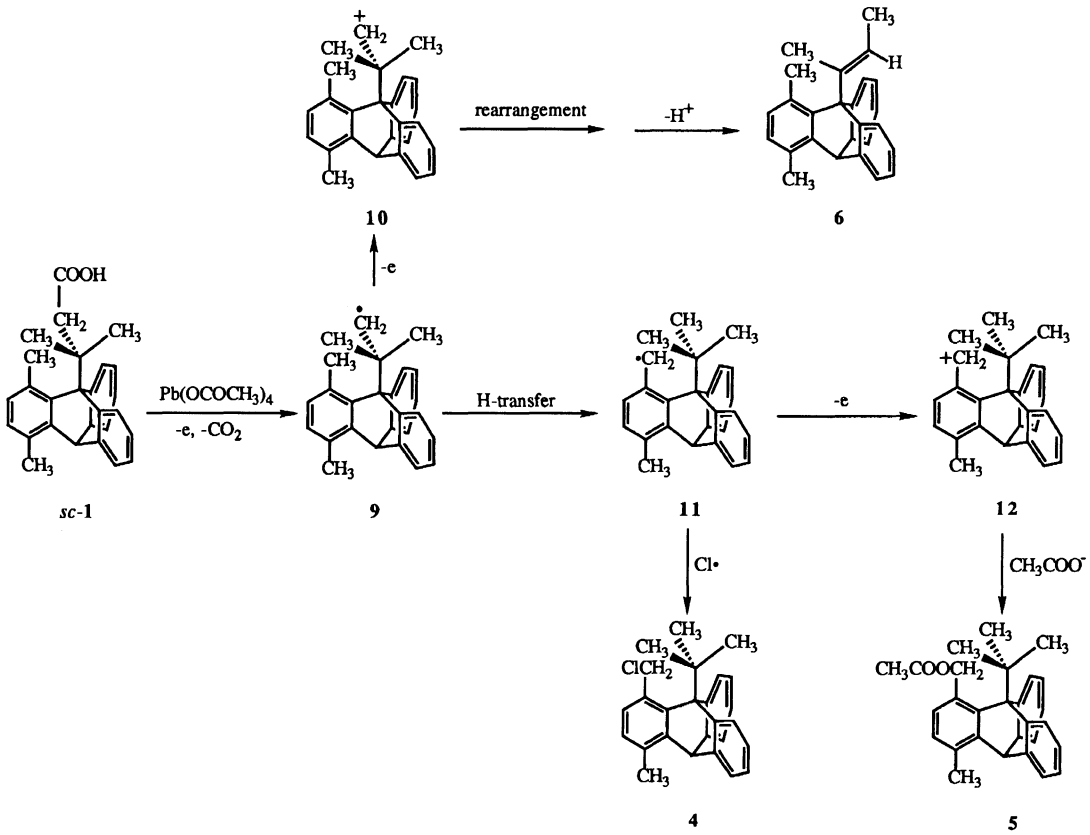
Formation of **5** from *sc*-**1** indicates that the radical **11** is long-lived to undergo oxidation with lead(IV) salt. This consequence can be attributed to two factors. The radical **11** is stable because of the benzylic nature and the radical may be protected against reactions because the site is sterically crowding. Effects of the concentration of chloride sources that decrease the formation of **5** at high concentration are attributed to the increase in reaction rates to form **4**.

The formation of the acetonyl ester (*sc*-**7**) is puzzling. There is no precedence in the literature. It is known that lead(IV) acetate gives trace of acetoxyacetone if acetone is present in the system.[20)] It is also known that lead(IV) acetate in acetic acid gives acetoxyacetic acid on heating.[21)] If acetone is formed in the reaction mixture, therefore, formation of *sc*-**7** would be rationalized. However, this reasoning has two drawbacks. One is that acetone may not be formed to an extent that will give 20—40% yields of *sc*-**7**. In addition, it is difficult to explain by this pathway why the formation of the acetonyl ester does not occur to *ap*-**1** but does so to *sc*-**1**. Works to elucidate the nature of the formation of *sc*-

Table 4. Selected Structural Parameters in Acetonyl *sc*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate[a)]

Bond distances (Å)			
C(9)–C(8a)	1.578(3)	C(9)–C(9a)	1.610(3)
C(9)–C(12)	1.564(3)	C(9)–C(19)	1.577(3)
C(10)–C(4a)	1.506(3)	C(10)–C(10a)	1.508(4)
C(10)–C(11)	1.506(4)	C(10)–C(20)	1.558(4)
C(19)–C(21)	1.563(4)	C(19)–C(22)	1.565(4)
Bond angles (°)			
C(9a)–C(1)–C(17)	131.9(2)	C(2)–C(1)–C(17)	110.7(2)
C(4a)–C(4)–C(18)	123.3(3)	C(3)–C(4)–C(18)	119.2(3)
C(8a)–C(9)–C(9a)	104.7(2)	C(8a)–C(9)–C(12)	103.2(2)
C(9a)–C(9)–C(12)	102.8(2)	C(8a)–C(9)–C(19)	113.2(2)
C(9a)–C(9)–C(19)	118.0(2)	C(12)–C(9)–C(19)	113.2(2)
Torsion angles (°)[b)]			
C(9)–C(19)–C(22)–C(23)	−167.3		
C(19)–C(22)–C(23)–O(2)	−82.9		
C(22)–C(23)–O(2)–C(24)	176.4		
C(23)–O(2)–C(24)–C(25)	−86.1		
O(2)–C(24)–C(25)–C(26)	−175.1		
Dihedral angles (°)[c)]			
Benzene A–Benzene B	123.0		
Benzene A–Benzene C	116.6		
Benzene B–Benzene C	120.4		

a) Values in parentheses are estimated standard deviations. b) Angles are calculated for $+sc$ isomer. c) Dihedral angles between average planes of the three benzene rings made by following carbons; Benzene A: C(1), C(2), C(3), C(4), C(4a), C(9a); Benzene B: C(5), C(6), C(7), C(8), C(8a), C(10a); Benzene C: C(11), C(12), C(13), C(14), C(15), C(16).



Scheme 5. Proposed pathways to the products from *sc*-**1**.

7 is under way.

Experimental

Melting points are not corrected. Elemental analyses were performed by a Perkin Elmer 240C analyzer. IR spectra, ^{1}H NMR, and ^{13}C NMR spectra were obtained on a Hitachi I-2000, on a Varian Gemini-300 at 300 MHz, and on the Varian Gemini-300 at 75.5 MHz, respectively.

Chlorodecarboxylation. To a solution of 50.1 mg (1.30×10^{-4} mol) of 3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoic acid[3] in 7.4 mL of benzene, was added 64.5 mg (1.31×10^{-4} mol) of lead(IV) acetate after purging oxygen by argon. The mixture was stirred at room temperature until a clear yellow solution resulted and then heated under reflux after addition of 22.2 mg (5.23×10^{-4} mol) of lithium chloride for 3 h. The mixture was cooled and washed with water. The water layer was extracted with dichloromethane and the combined organic layer was evaporated in vacuo after drying. The formation ratio of the products was determined at this stage by ^{1}H NMR spectra and the detailed ratios were obtained after chromatography described below.

The similar treatment was carried out for other cases using other ratios of lithium chloride and benzyltriethylammonium chloride. In the case of lithium chloride, a part of it remained undissolved in every case, whereas benzyltriethylammonium chloride formed a clear solution until 4 mol of it was added to 1 mol of the substrate and a part of it remained undissolved in the case of 10 molar excess.

Unreacted carboxylic acid was recovered mostly by treating the product with dichloromethane-hexane. In the above case, 65% of the starting material was recovered. A mixture of other products was chromatographed on silica gel (1 : 2 dichloromethane–hexane eluent) and a mixture of *ap*-chloride (*ap*-**2**) and the 5-membered ring compound (**3**), which was identified by comparison of the spectra with the authentic specimen,[8] was obtained. Crystals were allowed to deposit from a dichloromethane-hexane solution and were recrystallized from tetrahydrofuran-hexane to give pure *ap*-chloride (*ap*-**2**). Mp 261—262 °C. Found: C, 83.72; H, 6.67%. Calcd for $C_{26}H_{25}Cl$: C, 83.74; H, 6.76%. ^{1}H NMR ($CDCl_3$) δ=2.35, (6H, s), 2.49 (3H, s), 2.65 (3H, s), 4.67 (2H, s), 5.59 (1H, s), 6.75 (2H, s), 6.99—7.02 (4H, m), 7.37—7.40 (2H, m), 7.80—7.83 (2H, m).

The ^{1}H NMR data of the other product in the mixture were identical with those of the cyclized compound **3** which had been published.[8]

Benzyl *ap*-3-(1,4-dimethyl-9-triptycyl)-3-methylbutanoate was easily separated by chromatography from compounds *ap*-**2** and **3**. Its mp and spectral data were identical with those of independently prepared specimen shown below.

sc-Carboxylic acid was treated similarly. Chromatography on silica gel (1 : 4 dichloromethane–hexane eluent) afforded a mixture of the chloride and the olefin, the acetate, and the acetonyl ester in this order. The starting carboxylic acid was recovered in 60% yield.

The chloride (**4**) was purified by recrystallization from dichloromethane–hexane, mp 236—241 °C. Found: C, 83.55; H, 6.93%. Calcd for $C_{26}H_{25}Cl$: C, 83.74; H, 6.76%. ^{1}H NMR ($CDCl_3$) δ=2.10 (3H, s), 2.27 (6H, s), 2.52 (3H, s), 5.09 (2H, s), 5.59 (1H, s), 6.90 and 7.13 (2H, ABq, J=7.9 Hz), 6.99—7.02 (4H, m), 7.36—7.38 (2H, m), 7.88—7.91 (2H, m).

***sc*-9-(2-Chloro-1,1-dimethylethyl)-1,4-dimethyltriptycene (*sc*-2).** A solution of 330 mg (0.885 mmol) of *ap*-**2** in 10.0 mL of tetralin was heated under reflux for 17 h. After being cooled, the solvent was distilled under reduced pressure and the residue (*ap* : *sc*=ca. 1 : 1) was submitted to chromatography on alumina. Attempted separations of the isomers by high performance chromatography were unsuccessful. Thus the residue was separatred into *ap*-**2** and *sc*-**2** by repeated fractional crystallization from hexane, in which *ap*-isomer was less soluble. The *sc*-isomer was obtained in ca. 10% yield, mp 215.5—217.5 °C. Found: C, 83.73; H, 6.78%. Calcd for $C_{26}H_{25}Cl$: C, 83.74; H, 6.76%. ^{1}H NMR ($CDCl_3$) δ=2.17 (3H, s), 2.24 (3H, s), 2.53 (3H, s), 2.61 (3H, s), 4.55 and 5.01 (2H, ABq, J=12.1 Hz), 5.59 (1H, s), 6.79 and 6.82 (2H, ABq, J=7.5 Hz), 6.98—7.01 (4H, m), 7.34—7.40 (2H, m), 7.78—7.86 (2H, m).

1-Acetoxymethyl-9-*t*-butyl-4-methyltriptycene (5). To a solution of 50 mg (0.13 mmol) of the chloride **4** in 20 mL of acetic acid, was added 40 mg (0.20 mmol) of silver tetrafluoroborate and the mixture was stirred at room temperature for 2 h. The precipitate was removed by filtration and the filtrate was poured into water. The organic materials were extracted with dichloromethane and the solvent was evaporated from the extract. The product was purified by recrystallization from dichloromethane–hexane, mp 200—201 °C. Found: C, 84.54; H, 7.29%. Calcd for $C_{28}H_{28}O_2$: C, 84.81; H, 7.12%. ^{1}H NMR ($CDCl_3$) δ=2.02 (3H, s), 2.09 (3H, s), 2.21 (6H, s), 2.53 (3H, s), 5.47 (2H, s), 5.60 (1H, s), 6.90 and 6.97 (2H, ABq, J=8.0 Hz), 6.97—7.02 (4H, m), 7.36—7.39 (2H, m), 7.88—7.90 (2H, m).

Acetonyl 3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate (7). A mixture of 200 mg (0.52 mmol) of *sc*-**1** in 5 mL of tetrahydrofuran and 14 mg (0.58 mmol) of sodium hydride (60% oil suspension) was stirred for 1 h at room temperature and then 45 μL (0.57 mmol) of chloroacetone was added to the mixture. The whole was heated under reflux for 5 d. The mixture was quenched with 5 mL of water and was extracted with dichloromethane. The extract was dried and the solvent was evaporated. The residue was chromatographed on silica gel with 1 : 2 hexane–dichloromethane eluent. The product was obtained in 30% yield with recovery of *sc*-**1** in 45% yield. *sc*-**7** was recrystallized from dichloromethane–hexane, mp 213.5—214.5 °C. Found: C, 82.10; H, 6.78%. Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.89%. ^{1}H NMR ($CDCl_3$) δ=2.25 (3H, s), 2.29 (3H, s), 2.34 (3H, s), 2.53 (3H, s), 2.74 (3H, s), 3.80 and 3.96 (2H, ABq, J=16.1 Hz), 4.79 and 4.85 (2H, ABq, J=16.8 Hz), 5.59 (1H, s), 6.78 (2H, s), 6.96—7.03 (4H, m), 7.33—7.39 (2H, m), 7.83—7.87 (1H, m), 7.90—7.93 (1H, m). ^{13}C NMR ($CDCl_3$) δ=20.0, 26.2, 28.0, 31.7, 33.8, 35.7, 44.7, 52.5, 68.3, 70.4, 123.7, 123.8, 124.7, 125.1, 127.3, 127.6, 127.7, 129.6, 130.6, 131.6, 143.5, 144.6, 147.2, 147.9, 148.2, 172.1, 201.3. Two more aromatic carbons were not detected due to overlaps. IR ($CHCl_3$) 1216 and 1732 cm^{-1}.

ap-**7** was prepared similarly from *ap*-**1** but 18 h heating gave a satisfactory result. Yield 74%, mp 210.5—212.0 °C. Found: C, 82.10; H, 6.78%. Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.89%. ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s), 2.41 (6H, s), 2.49 (3H, s), 2.67 (3H, s), 3.71 (2H, s), 4.79 (2H, s), 5.59 (1H, s), 6.75 (2H, s), 6.98—7.04 (4H, m), 7.36—7.40 (2H, m), 7.86—7.90 (2H, m).

Benzyl *ap*-3-(1,4-Dimethyl-9-triptycyl)-3-methylbutanoate. A solution of 100 mg (0.26 mmol) of the *ap*-

acid (**1**) and 0.30 mL (3.5 mmol) of oxalyl dichloride in 10 mL of benzene was stirred for 2 h at room temperature and the solvent and volatile materials were evaporated in vacuo. The residue was taken up in 5.0 mL of tetrahydrofuran and to the solution were added 21 μL (0.26 mmol) of pyridine and 27 μL (0.26 mmol) of benzyl alcohol. The mixture was stirred for 2 h at room temperature, diluted with 10 mL of water, and extracted with dichloromethane. Solvent was evaporated after drying and the residue was submitted to preparative TLC on silica gel (1 : 1 hexane–dichloromethane eluent). The desired product was obtained in 83% yield and was purified by recrystallization from methanol, mp 143—144 °C. Found: C, 86.16; H, 6.84%. Calcd for $C_{34}H_{32}O_2$: C, 86.41; H, 6.82%. ^{1}H NMR ($CDCl_3$) δ=2.35 (6H, s), 2.49 (3H, s), 2.64 (3H, s), 3.63 (2H, s), 5.28 (2H, s), 5.58 (1H, s), 6.74 (2H, s), 6.94—7.06 (4H, m), 7.32—7.50 (7H, m), 7.81—7.90 (2H, m).

X-Ray Crystallography.[22] A Crystal used for the X-ray measurement was grown from hexane–dichloromethane solution and its size was 0.45×0.40×0.25 mm^3. X-Ray data were collected on a MAC Science MXC18 four circle diffractometer with Mo $K\alpha$ radiation (λ=0.71073 Å). The scan modes were the 2θ method ($2\theta<30°$) and the ω–2θ method ($2\theta>30°$). The scan rate was 3° min^{-1} and the scan range was calculated by $0.93°+0.35°\tan\theta$. The structure was solved by the direct method (MULTAN78) and refined by the full-matrix least-squares method by using a CRYSTAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. No absorption correction was employed. Total number of measured unique reflection was 5274 within the range of $3°<2\theta<55°$ and 3077 reflections within $|F_o|>5\sigma(F_o)$ were used for the structure determination and refinement. The function minimized was $\Sigma[w(|F_o|^2-|F_c|^2)^2]$, where $w=[(\sigma_c|F_o|)^2+1.3\times10^{-5}|F_o|^2]^{-1}$. Formula $C_{30}H_{30}O_3$, F. W. 438.60, Monoclinic, Space group $P2_1/c$, a=16.413(3), b=16.270(3), c=8.707(2) Å, β=92.00(2)°, V=2323.7(9) Å^3, Z=4, D_c=1.25 g cm^{-3}, μ=0.43 cm^{-1}. R 0.058, R_w 0.042.

References

1) For Part 31 of the series, see: M. Ōki, K. Shionoiri, K. Otake, M. Ono, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **66**, 589 (1993).

2) A preliminary report has been published: M. Ōki, T. Okamoto, S. Toyota, K. Yonemoto, and G. Yamamoto, *Chem. Lett.*, **1990**, 199.

3) T. Tanaka, K. Yonemoto, Y. Nakai, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **61**, 3239 (1988).

4) M. Ōki, T. Tanuma, Y. Tanaka, and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **61**, 4309 (1988).

5) Y. Tanaka, G. Yamamoto, and M. Ōki, *Chem. Lett.*, **1989**, 2019.

6) M. Ōki, Y. Taguchi, S. Toyota, K. Yonemoto, and G. Yamamoto, *Chem. Lett.*, **1990**, 2209.

7) J. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972).

8) S. Toyota, M. Endo, M. Teruhi, M. Ōki, M. Yamasaki, and T. Shibahara, *Bull. Chem. Soc. Jpn.*, **66**, 2088 (1993).

9) M. Ōki, Y. Taguchi, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **65**, 2616 (1992).

10) M. Mikami, T. Toriumi, K. Konno, and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 2474 (1975).

11) N. Nogami, M. Ōki, S. Sato, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **55**, 3580 (1982).

12) M. Ōki, N. Takiguchi, S. Toyota, G. Yamamoto, and S. Murata, *Bull. Chem. Soc. Jpn.*, **61**, 4295 (1988).

13) Y. Tamura, H. Takizawa, G. Yamamoto, M. Ōki, and S. Murata, *Bull. Chem. Soc. Jpn.*, **63**, 2555 (1990).

14) R. Isaksson, M. Ōki, J. Sandström, M. Rachel Suissa, and S. Toyota, *Acta Chem. Scand.*, **47**, 570 (1993).

15) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 2500 (1965).

16) J. K. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

17) T. Ando, H. Yamataka, H. Morisaki, J. Yamawaki, J. Kuramochi, and Y. Yukawa, *J. Am. Chem. Soc.*, **103**, 430 (1981).

18) V. J. Shiner, Jr., and J. J. Tai, *J. Am. Chem. Soc.*, **103**, 436 (1981).

19) E. C. Janzen and A. C. Evans, *J. Am. Chem. Soc.*, **97**, 205 (1975).

20) O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

21) M. S. Kharasch, H. N. Friedländer, and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).

22) Tables of coordinates of all atoms, anisotropic thermal parameters of non-hydrogen atoms, and complete F_o-F_c data are deposited as Document No. 66058 at the Office of the Editor of Bull. Chem. Soc. Jpn.