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(3S)- and (3R)-1-Iriden-7-als with (3S)-7-
Chloro-1-iridenes. ^1H NMR Spectral
Differentiation of the Stereochemistry

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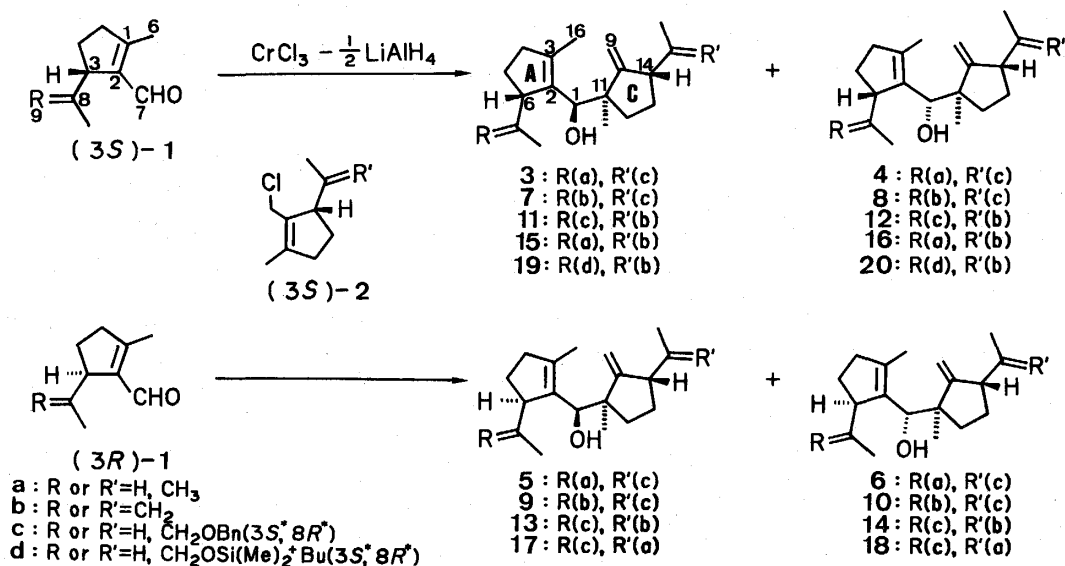
Synthetic Photochemistry. XLIII.¹⁾ Chromium(II) Chloride-Mediated Reductive Condensations of (3*S*)- and (3*R*)-1-Iriden-7-als with (3*S*)-7-Chloro-1-iridenes. ¹H NMR Spectral Differentiation of the Stereochemistry

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Dedicated to Professor Otohiko Tsuge on the occasion of his retirement

The chromium (II) chloride-mediated condensations of the several (3*S*)- and (3*R*)-1-iriden-7-als with (3*S*)-7-chloro-1-iridenes, were carried out. Due to a large steric hindrance from the C₃-side chain of the iridenes, stereochemistry of resultant condensates always possessed cis-geometry for the C-11 methyl and the C-14 C₃-substituents. The ¹H NMR chemical shift comparisons established the orientation of the hydroxyl groups on the C-1.

As previously reported,²⁾ the chromium (II) chloride-mediated condensations³⁾ of two optically active iridoid synthons (1*a*-1*d* and 2*a*-2*c*),⁴⁾ respectively afforded only an epimeric pair of



Scheme 1

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condensates. For examples, (3*S*)-1-iriden-7-al (**1a**) and (3*S*, 8*R*)-9-benzyloxy-7-chloro-1-iridene (**2c**) and (3*R*)-**1a** and (3*S*, 8*R*)-**2c** produced each two compounds (**3**, **4**, **5**, and **6**).²⁾

Since the stereochemistry of the C-11 methyl and C-14 isopropyl side chain for these products has been established by chemical transformations to be *cis*, we have utilized this strategy for synthesis of several stereochemically different tricyclic 5-8-5-membered higher terpenoids by combination with subsequent Cope rearrangement to appropriate carbon framework.^{5,6,7)} During the studies, we have carried out the condensations with various combinations, and obtained a diagnostic method of stereochemistries of condensates. Herein, we wish to report fundamental features of this versatile reductive condensation with combinations of (3*S*)- and (3*R*)-iridenals (**1a-1b**) with (3*S*)-chloroiridenes (**2a-2c**) and a way of stereochemical differentiation of the condensates.

Results and Discussions

Chromium(II) Chloride-Condensations of Optically-active Iridoids. First of all, when (3*S*)- and (3*R*)-1,8-iridadien-7-als (**1b**) were condensed respectively with (3*S*, 8*R*)-9-benzyloxy-7-chloro-1-iridene (**2c**) by means of chromium(II) chloride prepared from chromium(III) chloride and lithium aluminum hydride (LAH) in aprotic solvents (*N,N*-dimethylformamide (DMF) and/or tetrahydrofuran (THF)) under nitrogen atmosphere, two condensates (**7** and **8** from the former combination; **9** and **10** from the latter combination) were formed and isolated by means of silica-gel and high-pressure liquid chromatography. Similarly carried out were the reactions of (3*S*, 8*R*)- and (3*R*, 8*S*)-9-benzyloxy-1-iriden-7-als (**1c**) with (3*S*)-7-chloro-1,8-iridadiene (**2b**) to afford a similar set of four condensates (**11**, **12**, **13**, and **14**). Stereochemistry of these products was assigned on the basis of the NMR chemical shift comparisons to those of **3**, **4**, **5**, and **6**, since there are some diagnostic values for each type of condensates as discussed below. The reactions gave better results in DMF solutions than in THF as has been mentioned in the original report.³⁾

In addition, the reactions of (3*S*)-**1a** with (3*S*)-**2b**, (3*R*, 8*S*)-**1c** with (3*S*)-**2a**, and (3*S*, 8*R*)-9-[*t*-butyl(dimethyl)silyloxy]-1-iriden-7-al (**1d**) with (3*S*)-**2b** revealed the similar feature, i.e., only a formation of epimeric condensates (**15**, **16**, **17**, **18**, **19**, and **20**). Although combined yields of these epimers were sufficiently high, the ratio of each pair was variable. Control of this product ratio will be discussed elsewhere.

The product distributions of the reaction were compiled in Table 1.

Stereochemistries of the Condensates. The structures of these condensates were assigned mainly by ¹H- and ¹³C-NMR spectra. Tables 2 and 3 compare the chemical shifts of characteristic ¹H- and ¹³C-NMR signals.

The NMR chemical shifts suggested that the stable conformation of the (3*S*)-(3*S*)-condensates and (3*R*)-(3*S*)-condensates might be different. Thus, in the (3*S*)-(3*S*)-coupling products,

Table 1. Product distributions of reductive coupling reactions.

Aldehyde	Chloride	Conditions	β -Epimer (Yield/%)	α -Epimer (Yield/%)
(3 <i>S</i>)- 1b	(3 <i>S</i> , 8 <i>R</i>)- 2c	1b/2c =1.4, DMF	7 (60)	8 (6)
(3 <i>R</i>)- 1b	(3 <i>S</i> , 8 <i>R</i>)- 2c	1b/2c =1.5, DMF/THF=1 ^{a)}	9 (70)	10 (1)
(3 <i>S</i> , 8 <i>R</i>)- 1c	(3 <i>S</i>)- 2b	1c/2b =1, DMF/THF=2.5	11 (83)	12 (13)
(3 <i>R</i> , 8 <i>S</i>)- 1c	(3 <i>S</i>)- 2b	1c/2b =0.75, DMF/THF=0.5 ^{a)}	13 (88)	14 (7)
(3 <i>S</i>)- 1a	(3 <i>S</i>)- 2b	1a/2b =0.7, DMF/THF=0.5 ^{a)}	15 (70)	16 (3) ^{b)}
(3 <i>R</i> , 8 <i>S</i>)- 1c	(3 <i>S</i>)- 2a	1c/2a =0.75, DMF/THF=0.5 ^{a)}	17 (83)	18 (10)
(3 <i>S</i> , 8 <i>R</i>)- 1d	(3 <i>S</i>)- 2b	1d/2b =0.75, DMF/THF=0.5 ^{a)}	19 (93)	20 (6) ^{b)}

a) Me₂CHOH (0.25 0.5 eq. for CrCl₂) was added. b) not fully characterized.

Table 2. Characteristic ¹H NMR signals of condensates

	H-1	H-6	C-3 Me	C-11 Me	
<i>S-S</i> β -	3	4.31	2.82	1.68	1.15
	7	4.36	3.44	1.74	1.09
	11	4.42	2.82	1.66	1.22
	15	4.37	3.27	1.69	1.19
	19	4.45	— ^{a)}	1.64	1.22
<i>S-S</i> α -	4	4.26	2.48	1.88	0.92
	8	4.13	3.24	1.92	0.92
	12	4.29	2.60	1.87	0.98
<i>R-S</i> β -	5	4.04	2.45	1.90	1.09
	9	3.88	3.22	1.93	1.07
	13	4.16	2.58	1.88	1.13
	17	4.12	2.57	1.83	1.08
<i>R-S</i> α -	6	4.65	2.72	1.73	0.77
	10	4.55	3.38	1.73	0.87
	14	4.66	2.82	1.74	0.85
	18	4.66	2.82	1.72	0.79

a) Overlapped with other signals.

the ¹H NMR chemical shifts of C-11 methyls and C-3 methyls of the β -epimers were around δ =1.09–1.22 and 1.64–1.74, while those of α -epimers were 0.92–0.98 and 1.87–1.92. On the other hand, the corresponding chemical shifts of (3*R*)-(3*S*)-coupling products were δ =0.77–0.87 and 1.72–1.74 for α -epimers and 1.07–1.13 and 1.83–1.93 for β -epimers. Since the anisotropy from the C=C double bond and the substituent effect from the C-1 alcohol are primary factors to determine the chemical shifts of C-3 and C-11 methyls, the difference in chemical shifts may be interpreted in terms of different conformations. From these facts and molecular model considerations, conformations of four types of condensates were deduced as shown in Fig. 1. Common and characteristic features of these conformations are: i) C-1–H-1 bond is co-planar to C-3–C-2–C-6 plane to minimize the steric interactions between C-1 and C-2 (sp³-sp² relation), ii) C-ring locates opposite side of the C₃-substituent of A-ring to avoid non-bonded interactions between these two bulky groups, and iii) C-1–C-2 bond is put between C-12–C-11–C-18 which is the least steric gauche area around C-11. In the relation with these

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Table 3. Characteristic ¹³C NMR signals of condensates.

	C-1	C-11	C-9	C-16	C-18	
<i>S-S</i> β-	3	73.0	51.9	106.0	15.0	22.1
	7	75.0	52.0	106.2	15.3	23.6
	11	74.3	50.2	106.8	15.1	23.2
	15	73.4	51.6	107.4	15.0	22.2
	19	75.0	50.6	106.8	15.5	23.9
<i>S-S</i> α-	4	75.1	54.0	104.4	16.8	25.1
	8	75.2	53.8	104.5	16.5	25.0
	12	74.9	52.9	105.4	16.9	25.1
<i>R-S</i> β-	5	74.9	52.7	105.9	16.9	23.5
	9	75.1	52.7	106.4	16.7	23.3
	13	75.4	51.7	106.8	17.0	24.1
	17	75.0	52.6	105.5	17.0	23.6
<i>R-S</i> α-	6	75.2	52.5	104.0	15.0	25.4
	10	75.9	52.2	104.6	15.0	25.9
	14	75.5	50.4	104.4	15.0	25.8
	18	75.4	51.3	103.1	14.9	25.6

conformational arguments, it is known that the Cope rearrangement of the (3*R*)-(3*S*)-condensates always occurs, via the chair transition state, under more mild conditions than that of the (3*S*)-(3*S*)-condensation, which, proceed via the boat transition state in most cases.⁸⁾ The conformations in Fig. 1 are consistent with these phenomena, i.e., only the C-1-C-11 bond rotations are required to get the transitional conformations, and with such motions, the boat

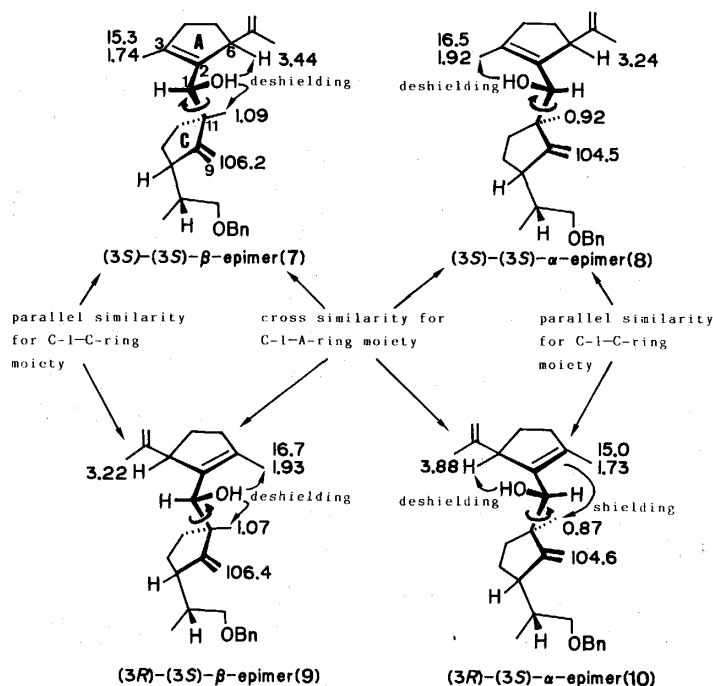


Fig. 1 Plausible conformation of each type of condensates.

7, 8, 9, and 10 are the representatives.

↷; motions for the transition states of Cope rearrangements.

transition states from (3*S*)-(3*S*)-condensates and the chair transition states from (3*R*)-(3*S*)-condensates are actually obtained.

In these conformations, C-1-C-ring moiety of (3*S*)-(3*S*)- β -epimer is pseudo-identical with that of (3*R*)-(3*S*)- β -epimer. And, both α -epimers of (3*S*)-(3*S*)- and (3*R*)-(3*S*)-series are also in similar relation with each other (parallel similarity). On the other hand, C-1-A-ring moiety of (3*S*)-(3*S*)- β -epimer is clearly different from that of (3*R*)-(3*S*)- β -epimer, but has pseudo-enantiomeric relation with that of (3*R*)-(3*S*)- α -epimer. Again, a similar cross-relation is also recognized between C-1-A-ring moiety of (3*S*)-(3*S*)- α -epimer and (3*R*)-(3*R*)- β -epimer (cross similarity).

Therefore, the above mentioned observations on the chemical shifts of C-3 and C-11 methyl groups are interpreted reasonably; i.e., C-11 methyls of (3*S*)-(3*S*)- β -epimer and (3*R*)-(3*S*)- β -epimer (parallel similarity on C-ring substituents) and C-3 methyls of (3*S*)-(3*S*)- α -epimer and (3*R*)-(3*S*)- β -epimer (cross similarity on A-ring substituents) appear at lower field because of the anisotropic deshielding effect of syn-oriented C-1 hydroxyl group. C-11 Methyls of (3*R*)-(3*S*)- α -epimers appear at slightly higher field than those of (3*S*)-(3*S*)- α -epimers, because the formers receive additional shielding effect from the C=C bond (C-2-C-3) which is expected only in the conformation of (3*R*)-(3*S*)- α -epimer.

The cross similarity on A-ring substituents is also recognized in the ¹H NMR chemical shifts of H-3's (lower in (3*S*)-(3*S*)- β -epimer and (3*R*)-(3*S*)- α -epimer) and ¹³C NMR chemical shifts of C-3 methyls (C-16; lower in (3*S*)-(3*S*)- α -epimer and (3*R*)-(3*S*)- β -epimer). While, the ¹³C NMR chemical shifts of C-9 exocyclic methylene carbons (lower in β -epimers of both series) and C-11 methyls (C-18; lower in α -epimers of both series) are the additional proof for the parallel similarity of C-ring substituents.

Since the conformations of condensates should receive little effects from the substituents on C₃-side chains of A-and C-rings, the chemical shifts of certain substituents have diagnostic features for the stereochemical determinations of various condensates. Especially, the combinations of ¹H NMR chemical shifts of C-3 methyls and C-11 methyls are useful, because the former value reveals the relation of C-1-A-ring moiety and the latter value reveals the relation of C-1-C-ring moiety. With this combination, it would be possible to determine the structure of condensates, even if the starting material were racemic. An example of this category will be described elsewhere.

Conclusion. In general, determination of the stereostructures of R-CH-X-R' (such as the dimeric condensates described in this paper), where R and R' represent groups having asymmetric carbons and R or R' is linked to the CH-X segment with quaternary carbon, is rather difficult. However, since we have started from the enantiomerically pure compounds with known absolute configurations, we could have unambiguously deduced the configurations. And it is rather remarkable that the relative geometry to the secondary hydroxyl group (X=OH) has provided such a clear NMR chemical shift difference.

Experimental

Elemental analyses were performed by Miss S. Hirashima, of this Institute. The NMR spectra were measured in CDCl₃ with a JEOL FX 100 Spectrometer, and the chemical shift were expressed in δ values. The mass spectra were measured with a JEOL 01SG-2 Spectrometer. The IR spectra were taken as liquid films or KBr disks using a Jasco IR-A 102 Spectrometer. The optical rotations were measured with a Union Model PM-101 apparatus. The solvents were carefully dried and distilled immediately before the use under N₂ atmosphere, and they were, therefore, anhydrous.

General Procedure for CrCl₂-mediated Coupling Reactions of (3*S*)- and (3*R*)-Iridenals with (3*S*)-Chloroiridenes. A THF suspension (15 cm³) containing CrCl₃ (1 g; 2.4 eq. for the chloroiridene) was reduced with LAH (0.5 eq. for CrCl₃) at 0°C. After stirring for a while at room temperature, the resultant black suspension was diluted with DMF when a mixed solvent of THF and DMF was used for the reaction. When DMF was the solvent, THF was removed in vacuo prior to the addition of DMF. Then, Me₂CHOH (if required), a DMF solution of the iridinal, and a DMF solution of the chloroiridene, were added successively. The mixture was then stirred at room temperature until the chloroiridene was consumed completely. In general, when DMF/THF ratio is higher, the reaction proceeds more rapidly. The mixture was then diluted with water and extracted with ether. Epimeric condensates were separated and purified by silica-gel column chromatography. Occasionally, HPLC (Micropolasil) was necessary for complete separation of the epimers.

Condensation of (3*S*)-1b with (3*S*, 8*R*)-2c. Formation of 7 and 8. (3*S*)-1b (1.25 g; 8.36 mmol) was condensed with (3*S*, 8*R*)-2c (1.71 g; 5.92 mmol) in DMF (50 cm³) to afford 7 [a colorless oil, 2.45 g; 60%. Found: C, 82.19; H, 9.95%. Calcd for C₂₇H₃₈O₂: C, 82.18; H, 9.71%. [α]_D²⁰: -48.2° (c 2.28, CHCl₃). ¹H NMR δ =1.08 (3H, d, *J*=7 Hz), 1.09 (3H, s), 1.70 (3H, br s), 1.74 (3H, br s), 3.19 (1H, t, *J*=8.5 Hz), 3.44 (1H, br m), 3.47 (1H, dd, *J*=8.5, 4 Hz), 4.36 (1H, br s), 4.42 (1H, d, *J*=12 Hz), 4.47 (1H, d, *J*=12 Hz), 4.67 (1H, m), 4.75 (1H, m), 4.88 (1H, d, *J*=2.5 Hz), 5.02 (1H, d, *J*=3 Hz), and 7.26 (5H, br s). ¹³C NMR δ =15.3 (q), 17.2 (q), 20.5 (q), 23.6 (t), 25.1 (t), 29.4 (t), 34.9 (t), 35.3 (d), 37.1 (t), 48.4 (d), 52.0 (s), 54.0 (d), 72.8 (2C, t), 75.0 (d), 106.2 (t), 109.1 (t), 127.2 (3C, d), 128.1 (2C, d), 136.1 (s), 138.3 (s), 138.7 (s), 151.7 (s), and 160.3 (s). IR ν : 3590, 2955, 2945, 2875, 1640, 1453, 1370, 1100, 892, 732, and 695 cm⁻¹] and 8 [a colorless oil, 0.15 g; 6%. Found: C, 82.25; H, 9.88%. [α]_D²⁰: -28.5° (c 2.00, CHCl₃). ¹H NMR δ =0.92 (3H, s), 1.11 (3H, d, *J*=7 Hz), 1.66 (3H, br s), 1.92 (3H, br s), 3.22 (1H, t, *J*=8.5 Hz), 3.24 (1H, br m), 3.48 (1H, dd, *J*=8.5, 4 Hz), 4.13 (1H, br s), 4.42 (1H, d, *J*=12 Hz), 4.47 (1H, d, *J*=12 Hz), 4.71 (2H, br s), 4.90 (1H, d, *J*=2.5 Hz), 4.95 (1H, d, *J*=3 Hz), and 7.27 (5H, br s). ¹³C NMR δ =16.5 (q), 17.1 (q), 19.4 (q), 25.0 (q), 25.1 (t), 28.4 (t), 32.7 (t), 34.7 (d), 39.1 (t), 49.7 (d), 53.8 (s), 59.1 (d), 72.7 (t), 73.0 (t), 75.2 (d), 104.5

(t), 110.8 (t), 127.4 (3C, d), 128.2 (2C, d), 135.5 (s), 138.2 (s), 138.8 (s), 148.4 (s), and 160.4 (s). IR ν : 3590, 2960, 2875, 1642, 1455, 1374, 1100, 885, and 692 cm^{-1}].

Condensation of (3R)-1b with (3S, 8R)-2c. Formation of 9 and 10. (3R)-1b (6.10 g; 40.5 mmol) was condensed with (3S, 8R)-2c (7.55 g; 27 mmol) in a 1:1-mixture of DMF and THF (200 cm^3) containing Me_2CHOH (2.5 cm^3) to afford **9** [colorless prisms, mp 56.5–57.5°C, 7.45 g; 70%. Found: C, 82.37; H, 9.74%. Calcd for $\text{C}_{27}\text{H}_{38}\text{O}_2$: C, 82.18; H, 9.71%. $[\alpha]_{\text{D}}^{19}$: -144.9° (c 2.07, CHCl_3). ^1H NMR δ =1.07 (3H, s), 1.09 (3H, d, $J=7$ Hz), 1.62 (3H, br s), 1.93 (3H, br s), 3.18 (1H, t, $J=8.5$ Hz), 3.22 (1H, br m), 3.45 (1H, dd, $J=8.5$, 4 Hz), 3.88 (1H, br s), 4.42 (1H, d, $J=12$ Hz), 4.46 (1H, d, $J=12$ Hz), 4.64 (1H, br s), 4.67 (1H, m), 4.93 (1H, d, $J=2.5$ Hz), 4.99 (1H, d, $J=3$ Hz), and 7.27 (5H, m). ^{13}C NMR δ =16.7 (q), 17.2 (q), 19.3 (q), 23.3 (q), 25.3 (t), 28.5 (t), 34.7 (t), 35.4 (d), 39.1 (t), 48.3 (d), 52.7 (s), 58.8 (d), 72.8 (t), 73.1 (t), 75.1 (d), 106.4 (t), 110.9 (t), 127.5 (d), 127.6 (2C, d), 128.4 (2C, d), 136.0 (s), 139.0 (s), 139.1 (s), 148.8 (s), and 160.6 (s). IR ν : 3515, 2950, 2860, 1639, 1444, 1365, 1084, 1074, 881, and 727 cm^{-1}] and **10** [a colorless oil, 110 mg; 1%. Found: C, 82.09; H, 9.77%. $[\alpha]_{\text{D}}^{18}$: -106.4° (c 1.25, CHCl_3). ^1H NMR δ =0.87 (3H, s), 1.11 (3H, d, $J=7$ Hz), 1.73 (6H, br s), 2.22 (1H, d, $J=5$ Hz), 3.21 (1H, t, $J=8.5$ Hz), 3.38 (1H, br m), 3.48 (1H, dd, $J=8.5$, 3.5 Hz), 4.41 (1H, d, $J=12$ Hz), 4.48 (1H, d, $J=12$ Hz), 4.55 (1H, d, $J=5$ Hz), 4.65 (1H, m), 4.73 (1H, m), 4.93 (1H, d, $J=2.5$ Hz), 4.97 (1H, d, $J=3$ Hz), and 7.27 (5H, br s). ^{13}C NMR δ =15.0 (q), 17.3 (q), 20.2 (q), 25.5 (t), 25.9 (q), 29.6 (t), 33.2 (t), 34.4 (d), 37.3 (t), 50.0 (d), 52.2 (s), 53.8 (d), 72.9 (t), 73.1 (t), 75.9 (d), 104.6 (t), 109.6 (t), 127.5 (d), 127.6 (2C, d), 128.5 (2C, d), 135.5 (s), 139.1 (s), 139.6 (s), 152.3 (s), and 160.7 (s). IR ν : 3565, 2950, 2865, 1640, 1454, 1369, 1100, 890, 735, and 697 cm^{-1}].

Condensation of (3S, 8R)-1c with (3S)-2b. Formation of 11 and 12. (3S, 8R)-1c (11 g; 38.2 mmol) was condensed with (3S)-2b (6.03 g; 39.7 mmol) in a 5:2-mixture of DMF and THF (530 cm^3) to afford **11** [a colorless oil, 10.28 g; 83%. Found: C, 82.38; H, 9.60%. Calcd for $\text{C}_{27}\text{H}_{38}\text{O}_2$: C, 82.18; H, 9.71%. $[\alpha]_{\text{D}}^{20}$: -22.5° (c 2.04, CHCl_3). ^1H NMR δ =0.84 (3H, d, $J=7$ Hz), 1.22 (3H, s), 1.62 (3H, br s), 1.66 (3H, br s), 2.82 (1H, br m), 2.90 (1H, br m), 3.21 (1H, dd, $J=9$, 4 Hz), 3.35 (1H, t, $J=9$ Hz), 3.93 (1H, br s), 4.38 (1H, d, $J=12$ Hz), 4.42 (1H, s), 4.44 (1H, d, $J=12$ Hz), 4.76 (3H, m), 5.09 (1H, m), and 7.23 (5H, br s). ^{13}C NMR δ =15.1 (q), 17.8 (q), 18.1 (q), 21.6 (t), 23.2 (q), 28.2 (t), 35.3 (d), 35.5 (t), 37.4 (t), 50.2 (s), 51.5 (d), 53.8 (d), 72.7 (t), 73.4 (t), 74.3 (d), 106.8 (t), 112.5 (t), 127.6 (d), 127.8 (2C, d), 128.2 (2C, d), 136.9 (s), 137.8 (2C, s), 146.4 (s), and 161.1 (s). IR ν : 3460, 2960, 2880, 1645, 1455, 1375, 1098, 1079, 1030, 1021, 1000, 890, 735, and 699 cm^{-1}] and **12** [a colorless oil, 1.56 g; 13%. Found: C, 82.12; H, 9.87%. $[\alpha]_{\text{D}}^{20}$: -60.9° (c 1.87, CHCl_3). ^1H NMR δ =0.98 (3H, s), 1.00 (3H, d, $J=7$ Hz), 1.62 (3H, br s), 1.87 (3H, br s), 2.60 (1H, br m), 3.17 (1H, dd, $J=9$, 7 Hz), 3.20 (1H, br m), 3.41 (1H, dd, $J=9$, 6 Hz), 4.29 (1H, br s), 4.42 (2H, br s), 4.79 (2H, m), 4.83 (1H, d, $J=2.5$ Hz), 4.90 (1H, d, $J=3$ Hz), and 7.26 (5H, br s). ^{13}C NMR δ =16.9 (q), 17.3 (q), 18.0 (q), 23.6 (t), 25.1 (q), 28.2 (t), 33.5 (t), 35.7 (d), 39.4 (t), 52.9 (s), 54.9 (d), 55.1 (d), 72.9 (t), 73.3 (t), 74.9 (d),

105.4 (t), 112.9 (t), 127.5 (d), 127.7 (2C, d), 128.3 (2C, d), 136.5 (s), 137.0 (s), 138.4 (s), 146.0 (s), and 160.1 (s). IR ν : 3590, 3400, 2965, 2880, 1642, 1455, 1372, 1100, 1030, 890, 732, and 695 cm⁻¹].

Condensation of (3*R*, 8*S*)-1c with (3*S*)-2b. Formation of 13 and 14. (3*R*, 8*S*)-1c (15.5 g; 60 mmol) was condensed with (3*S*)-2b (13.65 g; 80 mmol) in a 1:2-mixture of DMF and THF (840 cm³) containing Me₂CHOH (3.1 cm³) to give **13** [a colorless oil, 20.9 g; 88%. Found: C, 82.28; H, 9.62%. Calcd for C₂₇H₃₈O₂: C, 82.18; H, 9.71%. [α]_D²⁰: -15.8° (c 2.65, CHCl₃). ¹H NMR δ =0.94 (3H, d, *J*=7 Hz), 1.13 (3H, s), 1.3–1.9 (7H, m), 1.61 (3H, br s), 1.88 (3H, br s), 2.0–2.3 (3H, m), 2.58 (1H, br m), 3.05 (1H, br m), 3.17 (1H, dd, *J*=9, 7 Hz), 3.36 (1H, dd, *J*=9, 6 Hz), 4.16 (1H br s), 4.41 (2H, s), 4.77 (3H, m), 4.99 (1H, d, *J*=3 Hz), and 7.27 (5H, br s). ¹³C NMR δ =17.0 (q), 17.2 (q), 18.1 (q), 23.3 (t), 24.1 (q), 28.4 (t), 34.5 (t), 35.2 (d), 39.1 (t), 51.7 (s), 54.2 (2C, d), 72.7 (t), 73.3 (t), 75.4 (d), 106.8 (t), 112.7 (t), 127.5 (d), 127.7 (2C, d), 128.3 (2C, d), 136.9 (s), 137.2 (s), 138.5 (s), 146.3 (s), and 160.0. IR ν : 3590, 3480, 2960, 2870, 1643, 1497, 1453, 1372, 1098, 889, 735, and 697 cm⁻¹] and **14** [a colorless oil, 1.66 g; 7.0%. [α]_D²⁷: +15.9° (c 1.33, CHCl₃). Found: C, 82.00; H, 9.67%. ¹H NMR δ =0.82 (3H, d, *J*=7 Hz), 0.85 (3H, s), 1.63 (3H, br s), 1.74 (3H, br s), 1.2–2.0 (5H, m), 2.0–2.4 (3H, m), 2.82 (2H, br m), 3.18 (1H, br m), 3.1–3.5 (2H, m), 3.95 (1H, br s), 4.32 (1H, d, *J*=12 Hz), 4.46 (1H, d, *J*=12 Hz), 4.66 (1H, br s), 4.82 (3H, br s), 4.98 (1H, d, *J*=3 Hz), and 7.24 (5H, br s). ¹³C NMR δ =15.0 (q), 17.9 (2C, q), 21.6 (t), 25.8 (q), 29.0 (t), 32.7 (t), 35.6 (d), 37.5 (t), 50.4 (s), 51.2 (d), 55.3 (d), 72.7 (t), 73.3 (t), 75.5 (d), 104.4 (t), 113.0 (t), 127.5 (d), 127.8 (2C, d), 128.2 (2C, d), 136.5 (s), 137.8 (s), 138.2 (s), 146.0 (s), and 161.6 (s). IR ν : 3460, 2960, 1645, 1605, 1587, 1497, 1453, 1095, 887, 734, and 697 cm⁻¹].

Condensation of (3*S*)-1a with (3*S*)-2b. Formation of 15 and 16. (3*S*)-1a (6.11 g; 35.8 mmol) was condensed with (3*S*)-2b (8.07 g; 53.0 mmol) in a 1:2-mixture of DMF and THF (450 cm³) containing Me₂CHOH (2.7 cm³) to afford **15** [a colorless oil, 7.19 g; 70%. Found: C, 83.02; H, 10.90%. Calcd for C₂₀H₃₂O: C, 83.27; H, 11.18%. [α]_D¹⁴: -65.5° (c 2.06, CHCl₃). ¹H NMR δ =0.73 (3H, d, *J*=7 Hz), 0.90 (3H, d, *J*=7 Hz), 1.19 (3H, s), 1.61 (3H, br s), 1.69 (3H, br s), 1.3–1.9 (7H, m), 2.0–2.6 (3H, m), 2.86 (1H, br m), 3.27 (1H, br m), 4.37 (1H, d, *J*=1 Hz), 4.80 (3H, m), and 5.04 (1H, d, *J*=3 Hz). ¹³C NMR δ =15.0 (q), 15.8 (q), 18.2 (q), 21.9 (q), 21.9 (t), 22.2 (q), 28.0 (t), 30.5 (d), 35.6 (t), 38.1 (t), 51.6 (s), 53.4 (d), 53.5 (d), 73.4 (d), 107.4 (t), 112.9 (t), 136.2 (s), 139.2 (s), 146.8 (s), and 161.8 (s). IR ν : 3550, 2955, 2860, 1640, 1465, 1370, 1050, and 855 cm⁻¹] and **14** [a colorless oil, 0.36 g; 3%] which was not fully characterized.

Condensation of (3*R*, 8*S*)-1c and (3*S*)-2a. Formation of 17 and 18. (3*R*, 8*S*)-1c (3.88 g; 15.0 mmol) was condensed with (3*S*)-2a (3.46 g; 20.0 mmol) in a 1:2-mixture of DMF and THF (210 cm³) containing Me₂CHOH (0.8 cm³) to afford **17** [a colorless oil, 4.94 g; 83%. Found: C, 81.83; H, 10.11%. Calcd for C₂₇H₄₀O₂: C, 81.77; H, 10.17%. [α]_D²⁰: -43.3° (c 1.20, CHCl₃). ¹H NMR δ =0.75 (3H, d, *J*=7 Hz), 0.93 (3H, d, *J*=7 Hz), 0.95 (3H, d, *J*=7 Hz), 1.08 (3H, s),

1.83 (3H, br s), 2.57 (1H, br m), 3.16 (1H, dd, $J=9, 7$ Hz), 3.55 (1H, dd, $J=9, 5.5$ Hz), 4.12 (1H, br s), 4.40 (2H, s), 4.81 (1H, d, $J=2$ Hz), 5.00 (1H, d, $J=2$ Hz), and 7.24 (5H, br s). ^{13}C NMR $\delta=16.5$ (q), 17.0 (q), 17.2 (q), 22.1 (q), 23.4 (2C, t), 23.6 (q), 29.0 (d), 34.4 (t), 35.2 (d), 39.1 (t), 50.6 (d), 52.6 (s), 54.3 (d), 72.7 (t), 73.3 (t), 75.0 (d), 105.5 (t), 127.5 (d), 127.6 (2C, d), 128.3 (2C, d), 136.8 (s), 137.0 (s), 138.5 (s), and 161.2 (s). IR ν : 3590, 3470, 2960, 2870, 1642, 1499, 1455, 1367, 1096, 1074, 1029, 733, and 697 cm^{-1}] and **18** [a colorless oil, 620 mg; 7.0%. Found: C, 81.52; H, 10.07%. ^1H NMR $\delta=0.79$ (3H, d, $J=7$ Hz), 0.79 (3H, s), 0.84 (3H, d, $J=7$ Hz), 0.98 (3H, d, $J=7$ Hz), 1.72 (3H, br s), 2.82 (1H, br m), 3.21 (1H, dd, $J=9, 4.5$ Hz), 3.35 (1H, dd, $J=9, 8.5$ Hz), 3.84 (1H, br s), 4.32 (1H, d, $J=12$ Hz), 4.44 (1H, d, $J=12$ Hz), 4.66 (1H, br s), 4.83 (1H, d, $J=3$ Hz), 4.99 (1H, d, $J=3$ Hz), and 7.24 (5H, br s). ^{13}C NMR $\delta=14.9$ (q), 16.2 (q), 17.8 (q), 21.7 (t), 22.1 (q), 23.5 (t), 25.6 (q), 27.7 (d), 32.3 (t), 35.6 (d), 37.5 (t), 51.1 (d), 51.3 (s), 52.0 (d), 71.7 (t), 73.3 (t), 75.4 (d), 103.1 (t), 127.5 (d), 127.7 (2C, d), 128.2 (2C, d), 136.8 (s), 137.8 (2C, s), and 162.2 (s). IR ν : 3460, 2960, 1645, 1456, 1369, 1205, 1095, 1078, 1029, 1001, 878, 735, and 698 cm^{-1}].

Condensation of (3S, 8R)-1d with (3S)-2b. Formation of 19 and 20. (3S, 8R)-1d (2.39 g; 8.47 mmol) was condensed with (3S)-2b (1.93 g; 11.29 mmol) in a 1:2-mixture of DMF and THF (120 cm^3) containing Me_2CHOH (0.52 cm^3) to give **19** [a colorless oil, 3.31 g; 93%. ^1H NMR $\delta=0.03$ (3H, s), 0.05 (3H, s), 0.80 (3H, d, $J=7$ Hz), 0.88 (9H, s), 1.22 (3H, s), 1.64 (6H, br, s), 2.1–2.3 (2H, br m), 2.6–3.3 (3H, m), 3.44 (1H, dd, $J=9, 4$ Hz), 3.53 (1H, dd, $J=9, 8$ Hz), 3.96 (1H, br s), 4.45 (1H, br, s), 4.7–4.8 (3H, m), and 5.10 (1H, m). ^{13}C NMR $\delta=-5.8$ (q), -5.6 (q), 15.5 (q), 17.5 (q), 18.1 (q), 18.4 (s), 21.3 (t), 23.9 (q), 26.0 (3C, q), 28.2 (t), 35.4 (t), 36.4 (d), 37.4 (t), 50.6 (s), 51.7 (d), 54.2 (d), 65.8 (t), 75.0 (d), 106.8 (t), 112.7 (t), 136.7 (s), 137.7 (s), 146.7 (s), and 161.3 (s). IR ν : 3450, 2950, 1650, 1470, 1380, 1261, 1072, 890, 840, and 670 cm^{-1}] and **20** [a colorless oil, 196 mg; 6%] which was not fully characterized.

References

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- 4) Notations with Roman characters represent a: 1-iridenes, b: 1, 8-iridadienes, c: 9-benzyloxy-1-iridenes, and d: 9-[t-butyl(dimethyl)silyloxy]-1-iridenes. The numbering of the carbon skeleton and the ring letters were shown in the scheme 1.
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- 7) N. Kato, H. Kataoka, S. Ohbuchi, S. Tanaka, and H. Takeshita, *J. Chem. Soc., Chem. Commun.*, **1988**, 354.
- 8) It can be pointed out that ease of the Cope rearrangement, as an electrocyclic reaction, must be judged primarily from the non-bonding interactions of the transition state conformer of reactants. The compounds, which give termolysates via different transition geometries, must also have the different geometries in the ground states.