A New Synthesis of α-Phenylsulfonyl-γ-lactones and Their Use for Syntheses of Actinidiolide Derivatives[1)]

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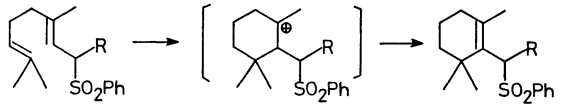
The acid-catalyzed cyclization of 2-phenylsulfonyl-4,8-dimethyl-3,7-nonadienoic acid (**5**) was performed by treatment with sulfuric acid-acetic acid and/or boron trifluoride in various aprotic solvents to afford 2,2,6-trimethyl-9-phenylsulfonyl-7-oxabicyclo[4.3.0]nonan-8-one (**4**) in 70—75% yield. Similarly, 2-phenylsulfonyl-2-(2,6,6-trimethyl-1,3-cyclohexadienyl)acetic acid provided 2,2,6-trimethyl-9-phenylsulfonyl-7-oxabicyclo[4.3.0]non-4-en-8-one (**7**) in 62% yield. The lactones **4a**, **4b**, and **7** were converted into dihydroactinidiolide, tetrahydroactinidiolide, and 4,5-dihydroactinidiolide. The reaction conditions and mechanism of the cyclization of **5** are discussed.

In connection with syntheses of terpenoids, the acid-catalyzed cyclization of functionalized polyisoprenoids has been reviewed.[2)] However, in spite of need for obtaining naturally occurring γ-lactones, very few satisfactory results have been obtained concerning one-step lactonization of acyclic polyolefinic carboxylic acids.[3)]

Reports have been given on a convenient preparation of 2-phenylsulfonyl-1,3,3-trimethylcyclohexene (**1a**) by the acid-catalyzed cyclization of 1-phenylsulfonyl-3,7-dimethylocta-2,6-diene (**2a**), as well as its use for the syntheses of terpenoids such as deoxytrisporone, vitamin A acid and ferruginol.[4)] On the cyclization of **2**, it was assumed that the reaction proceeds *via* the carbonium ion **3** which would undergo deprotonation or ring closure by intramolecular nucleophilic attack of another carbon-carbon double bond. This assumption prompted us to carry out one-step preparation of 2,2,6-trimethyl-9-phenylsulfonyl-7-oxabicyclo[4.3.0]nonan-8-one (**4**) from 2-phenylsulfonyl-4,8-dimethyl-3,7-nonadienoic acid (**5**). The presence of a phenylsulfonyl group at the terminal position of polyolefin chain allows the introduction of carboxyl group at the α-position, affording both α,β-unsaturated and saturated γ-lactones by either thermal elimination or reductive removal of the phenylsulfonyl group.



2a R=H b R=Alkyl — 3 — 1a b

This paper gives details on cyclization[5)] of **5** and 2-phenylsulfonyl-2-(2,6,6-trimethyl-1,3-cyclohexadienyl)-acetic acid (**6b**) along with a novel transformation of lactones **4a**, **4b**, and 2,2,6-trimethyl-9-phenylsulfonyl-7-oxabicyclo[4.3.0]non-4-en-8-one (**7**) into dihydroactinidiolide (**8**), isolated from Actinidia polygama Mig. (Matatabi),[6,7)] tetrahydroactinidiolide (**9a** and **9b**),[8)] and 4,5-dihydroactinidiolide (**10**).[9)]

Results and Discussion

Acid-catalyzed Lactonization of the Carboxylic Acids 5 and 6b. The carboxylic acids **5** and **6b** were easily prepared from the corresponding sulfones **2a** and **6a** by carboxylation.[10)] Treatment of **2a** with 2 equiv. of butyllithium in tetrahydrofuran at −70 °C followed with dry carbon dioxide yielded **5** in 99% yield. Similarly, **6b** was obtained in 96% yield.

Table 1. Cyclization of 5 with sulfuric acid

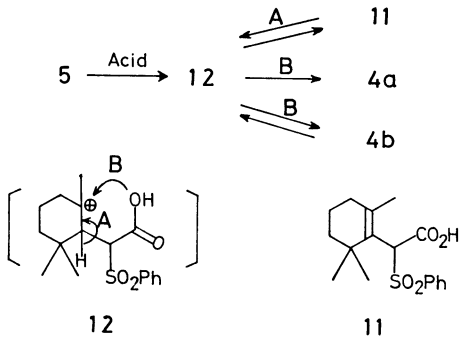
Entry	Ratio of acids[a)] H_2SO_4/AcOH	Temp[b)] °C	Product, %	
			4 (*cis*/*trans*)	**11**
1	1/1	12	64 (1.6)	26
2	4/1	5	66 (2.3)	3
3	4/1	20	66 (6.0)	0
4	1/0	5	75 (∞)[c)]	0

a) v/v. b) Reaction time 0.5 h. c) No *trans*-isomer obtained.

The acid-catalyzed lactonization of **5** was performed using protonic or Lewis acid (Table 1). Treatment of **5** with sulfuric and acetic acids (1:1) at 12 °C for 0.5 h provided **4** (64%) and **11** (26%). The product **4** consists of a mixture of *cis*- and *trans*-fused γ-lactones, which were separated by column chromatography and identified by a comparison with spectral data and also conversion of **4a** and **4b** into the corresponding tetrahydroactinidiolides **9a** and **9b** by reductive removal of the phenylsulfonyl group. The structure of **11** was confirmed by a comparison of the spectral data with those of the authentic sample prepared by the carboxylation of **1a**.

Increase of the concentration of sulfuric acid and/or the higher reaction temperature (Table 1, Runs 3—4) facilitates the formation of *cis*-lactone **4a**. In particular, the reaction of **5** in concd sulfuric acid at 5 °C gave **4a** in 75% yield as the sole product.

The carboxylic acid **11** was converted into **4** (**4a**/**4b**=4/1) in 45% yield on treatment with sulfuric and acetic acids (1:1) for 4 h. The *trans*-lactone **4b** undergoes complete isomerization to *cis*-lactone **4a** on treatment with sulfuric acid at 5 °C for 1 h. In strong acidic media the thermodynamically more stable *cis*-lactone **4a** would be produced preferentially to *trans*-isomer **4b**. Thus, it is assumed that the intermediate **12** would suffer either deprotonation to afford monocyclic carboxylic acid **11** (Path A in Scheme 1) or intramolecular nucleophilic attack by carboxyl group to produce a mixture of *cis*- and *trans*-lactones (Path B), although the mechanism of the concerted lactonization of **5** to *trans*-**4b** followed by isomerization of **4b** to **4a** *via* **12** could not be ruled out.



Scheme 1.

Among Lewis acids, boron trifluoride gave satisfactory results as shown in Table 2. Treatment of **5** with boron trifluoride in refluxing benzene for 1 h provided **4** (75%) and **11** (20%). Changes of solvents did not seriously affect the yield of **4**. Only carbon tetrachloride slightly improved the yield of *trans*-lactone **4b**.

Cyclization of the carboxylic acid **6b** with sulfuric and acetic acids (1:6) afforded *cis*-lactone **7** (62%). The stereochemistry of **7** was confirmed by the fact that hydrogenation of **7** with PtO_2 affords **4a** exclusively.

Preparation of Actinidiolide Derivatives. Many attempts have been made to synthesize **8** and related compounds **9a** and **9b**, because of its significant biological activity and importance as a strong fragrance for tea and tobacco. Photochemical oxidation of β-ionone derivatives,[11] β-carotenoids,[12] and retinal[13] gives **8** in poor yield. Another approach includes lactonization of homogeranic acid derived from 2,2,6-trimethylcyclohexanone resulting in unsatisfactory total yield.[14]

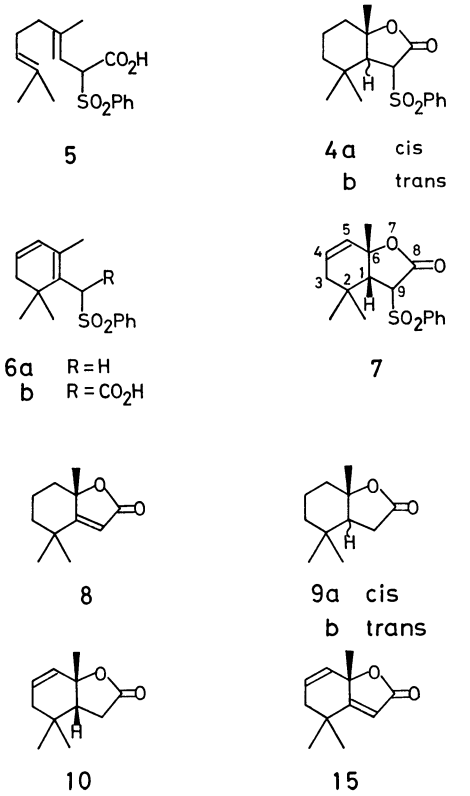


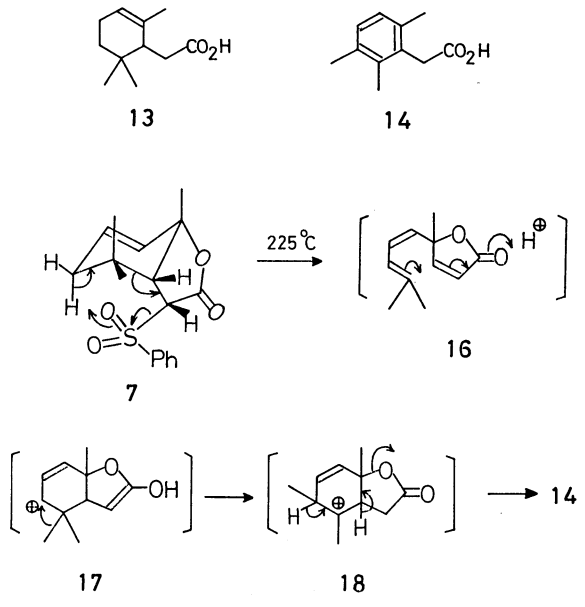
Table 2. Cyclization of **5** with boron trifluoride in various solvents

Entry	Solvent	Temp °C	Time h	Product, %	
				4 (*cis*/*trans*)	**11**
1	Toluene	reflux	1	73 (2.4)	3
2	Benzene	reflux	1	75 (2.4)	20
3	$CHCl_3$	reflux	1	71 (2.3)	26
4	CH_2Cl_2	reflux	1	70 (2.0)	21
5	CH_2Cl_2	0—4	168	71 (2.3)	21
6	CCl_4	reflux	1	55 (1.7)	12

The present attempt deals with a straightforward preparation of **8**, **9a**, **9b**, and **10** *via* the lactones **4** and **7**. Thermolysis of the lactone **4a** at *ca.* 300 °C afforded **8** (67%) and diphenyl disulfide (66%). The spectral data of **8** are in line with those reported.[6,9] Reduction of **4a** with Raney Ni W-2 in ethanol afforded *cis*-tetrahydroactinidiolide (**9a**) (84%). Similarly, **4b** yielded the *trans*-isomer **9b** (81%). The structure of both **9a** and **9b** were identified by a comparison of their spectral data.[15,16]

Reduction of **7** with potassium metal in liquid ammonia at −70 °C afforded **10** (91%)[9] and **13** (4%).[14e] Hydrogenation of the lactone **10** with Pd/C in methanol gave **9a** in 91% yield.

In contrast to the thermal elimination of phenylsulfonyl group of **4**, the lactone **7** gave **14** (75%) and diphenyl disulfide (65%) instead of actinidiolide (**15**), when **7** was heated to 225 °C. The thermal reaction of **7** can be initiated by the preferential 1,4-elimination of phenylsulfonyl group and allylic proton on C-3 as shown in Scheme 2. The incipient intermediate **16** might undergo recyclization producing **17**, which would be transformed into the stable aromatic compound **14** by subsequent Wagner-Meerwein rearrangement followed by deprotonation and aromatization.



Scheme 2.

Experimental

Melting points are uncorrected. IR spectra were determined with a JASCO IRA-1 infrared spectometer. NMR spectra were obtained at 60 MHz with a Hitachi R-24 spectrometer, chemical shift values being expressed in δ value (ppm) relative to Me_4Si in $CDCl_3$.

*2-Phenylsulfonyl-4,8-dimethyl-3,7-nonadienoic Acid (**5**).* To a stirred solution of 56 mg (0.2 mmol) of **2a** in 4 ml of dry THF was added dropwise 0.8 ml (0.4 mmol) of BuLi at −70 °C under N_2. After stirring at −70 °C for 5 min, dry CO_2 was introduced into the solution with vigorous stirring for 2.5 h. The mixture was concentrated to 1 ml under reduced pressure. The residue was dissolved in ether, the acidic products being extracted with saturated $NaHCO_3$. The combined $NaHCO_3$ extracts were acidified with 10% HCl. The organic material was extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed (SiO_2, hexane and then EtOH-CH_2Cl_2=4/1) to give 64 mg (99%) of **5** as a colorless liquid. Esterification of **5** with diazomethane gave 66 mg of the corresponding methyl ester. Methyl ester of **5**: IR (neat): 1745 (C=O), 1580, 1327, 1149 (SO_2) cm^{-1}; NMR : δ 7.32—7.99(m, 5, ArH), 5.26 (d, 1, J=11 Hz, CH=), 5.03(m, 1, CH=), 4.78 (d, 1, J=11Hz, $CHSO_2$), 3.75(s, 3, CH_3O), 1.90—2.19 (m, 4, CH_2), 1.70 (s, 3, CH_3), 1.60 (s, 3, CH_3), 1.51 (s, 3, CH_3). Found: C, 64.52; H, 7.30%. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19%.

*2-Phenylsulfonyl-2-(2,6,6-trimethyl-1,3-cyclohexadienyl)acetic Acid (**6b**).* The carboxylic acid **6b** was obtained in 96% yield as a slight yellow oil by a procedure similar to that for **5**. Methyl ester of **6b**: IR(neat): 1741 (C=O), 1320, 1145 (SO_2) cm^{-1}; NMR: δ 7.37—8.12 (m, 5, ArH), 5.79 (br s, 2, CH=), 4.89 (s, 1, CH), 3.66 (s, 3, CH_3O), 1.96—2.28 (m, 2, CH_2), 1.81 (s, 3, CH_3), 1.16 (s, 3, CH_3), 1.01 (s, 3, CH_3). Found: C, 64.93; H, 6.55%. Calcd for $C_{18}H_{22}O_4S$: C, 64.65: H, 6.63%.

*2-Phenylsulfonyl-2-(2,6,6-trimethyl-1-cyclohexenyl)acetic Acid (**11**).* Mp 182—182.5 °C; IR (Nujol): 1706 (C=O), 1325, 1150 (SO_2) cm^{-1}; NMR of methyl ester of **11**: δ 7.35—8.08 (m, 5, ArH), 4.70 (s, 1, CH), 3.70 (s, 3, CH_3O), 1.98—2.30 (m, 2, CH_2C=), 1.88 (s, 3, CH_3), 1.47—1.78 (m, 4, CH_2), 1.08(s, 3, CH_3), 0.89 (s, 3, CH_3). Found: C, 63.51; H, 6.92%. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88%.

*2,6,6-Trimethyl-9-phenylsulfonyl-7-oxabicyclo[4.3.0]nonan-8-one (**4**).* To a refluxing solution of 161 mg (0.5 mmol) of **5** in 6 ml of freshly distilled CH_2Cl_2 under N_2 was added BF_3 etherate (150 mg). After the mixture had been refluxed for 30 min, 100 mg of BF_3 etherate and after 30 min an additional 30 mg were added. The mixture was further refluxed for 1 h. After being cooled to room temperature and quenched with saturated $NaHCO_3$, the mixture was washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residual crystalline product was chromatographed (SiO_2, benzene–AcOEt=10:1) to give 121 mg (75%) of **4** (**4a**/**4b**=2.4/1) as colorless crystals. The $NaHCO_3$ solution was acidified with 5% HCl, the organic material being extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo* to yield 32 mg (20%) of **11** as crystals.

(**4a**): Mp 173.5—174.5 °C; IR (Nujol): 1770 (C=O), 1317, 1150 (SO_2) cm^{-1}; NMR: δ 7.35—8.07 (m, 5, ArH), 4.01 (d, 1, J=6 Hz, CHCO), 2.76 (d, 1, J=6 Hz, CH), 1.31—2.00 (m, 6, CH_2), 1.60(s, 3, CH_3), 1.14 (s, 3, CH_3), 1.06 (s, 3, CH_3). Found: C, 63.50; H, 7.03%. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88%.

(**4b**): Mp 131—132 °C; IR (Nujol): 1770 (C=O), 1305, 1145 (SO_2) cm^{-1}; NMR: δ 7.30—8.00 (m, 5, ArH), 4.17 (d, 1, J=13 Hz, CHCO), 2.78 (d, 1, J=13 Hz, CH), 1.25—2.05 (m, 6, CH_2), 1.41 (s, 3, CH_3), 1.34(s, 3, CH_3), 1.15 (s, 3, CH_3). Found: C, 63.16; H, 6.83%. Calcd for $C_{17}H_{22}O_4S$: C, 63.33; H, 6.88%.

*Cyclization of **4** with H_2SO_4.* 1 ml of ice-cooled concd H_2SO_4 was added dropwise to 75 mg (0.23 mmol) of **5**. After vigorous stirring at 0 °C for 1 h, the mixture was poured into 10 ml of ice water. The organic layer was extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (SiO_2, benzene) to give 56 mg (75%) of **4a**.

*2,2,6-Trimethyl-9-phenylsulfonyl-7-oxabicyclo[4.3.0]non-4-en-8-one (**7**).* To 50 mg (0.16 mmol) of **6b** was added dropwise 3.5 ml of an ice-cooled mixture of H_2SO_4 (0.5 ml) and AcOH (3 ml). After being stirred at room temperature for 18 h, the mixture was poured into 15 ml of ice water and the organic layer was extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (SiO_2, benzene–AcOEt=10/1) to give 31 mg (62%) of **7** as colorless crystals: mp 134—134.5 °C (benzene–hexane); IR (Nujol): 1769 (C=O), 1321, 1150 (SO_2) cm^{-1}; NMR: δ 7.35—8.10 (m, 5, ArH), 5.80 (br s. 2, CH=), 4.00 (d, 1, J=4 Hz, CHCO), 2.91 (d, 1, J=4 Hz, CH), 1.85—2.07 (m, 2, CH_2), 1.63 (s, 3, CH_3), 1.09 (s, 3, CH_3), 0.95 (s, 3, CH_3). Found: C, 63.58; H, 6.16%. Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29%.

*Isomerization of **4b** to **4a**.* 1 ml of ice-cooled concd H_2SO_4 was added dropwise to 35 mg (0.11 mmol) of **4** (**4a**/**4b**=1/2.3). After vigorous stirring at 0 °C for 1 h, the mixture was poured into ice water and the organic layer was extracted with AcOEt. The extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed (SiO_2, benzene) to give 31 mg (89%) of **4a** as colorless crystals.

*Hydrogenation of **7** to **4a**.* A suspension of 32 mg (0.1 mmol) of **7** and 10 mg of PtO_2 in 2 ml of dry MeOH was stirred vigorously at room temperature under H_2 for 12 h. The usual work-up and chromatography (SiO_2, benzene–AcOEt=10/1) yielded 31 mg (96%) of **4a** as colorless crystals.

*2,2,6-Trimethyl-7-oxabicyclo[4.3.0]non-9-en-8-one (Dihydroactinidiolide) (**8**).* Sulfone **4a** (40 mg, 0.12 mmol) in a glass tube (7ϕ, 25 cm) was refluxed in an air bath at 300—320 °C for 12 min, the volatile oil being collected. The oil was chromatographed (SiO_2, hexane–AcOEt=2/1) to give 15 mg (67%) of **8** as a colorless oil and 9 mg (66%) of diphenyl disulfide.

trans-*Tetrahydroactinidiolide (**9b**).* A suspension of 120 mg of Raney Ni W-2 and 37 mg (0.11 mmol) of **4b** in a mixture of 1.5 ml of EtOH and 1.5 ml of distilled water was refluxed at 110—120 °C for 10 h. After separation of Raney Ni through a short column, the organic phase was concentrated and chromatographed (SiO_2, benzene–AcOEt=10/1) to yield 17 mg (81%) of **9b** as a colorless oil.

cis-*Tetrahydroactinidiolide (**9a**).* Similarly, reduction of **4a** with Raney Ni W-2 provided **9a** in 84% yield.

*2,2,6-Trimethyl-7-oxabicyclo[4.3.0]non-4-en-8-one (**10**).* A few pieces of potassium metal (29 mg, 0.75 mmol) were added to a solution of **7** (80 mg, 0.25 mmol) in 1 ml of dry THF and 20 ml of liq ammonia at −70 °C. After 1 min, saturated NH_4Cl was added and then liq ammonia was evaporated at room temperature for 2 h. The residue was combined with 2 ml of 5% HCl and the organic substances were extracted with AcOEt. The extracts were washed with

brine, dried (Na_2SO_4), and concentrated under reduced pressure to yield 44 mg of colorless liquid which was chromatographed (SiO_2, benzene–AcOEt=30/1) to give 41 mg (91%) of **10** as a colorless liquid and 2 mg (4%) of **13**.

Hydrogenation of ***10***. A suspension of 7 mg of Pd/C and 37 mg (0.21 mmol) of **10** in 2 ml of dry MeOH was stirred under H_2 at room temperature for 12 h. After the usual work-up and chromatograph (SiO_2, benzene), 34 mg (91%) of **9a** was obtained as a colorless oil.

*2,3,6-Trimethylphenylacetic Acid (****14****).* Lactone **7** (48 mg, 0.15 mmol) was heated to 225 °C in a glass tube settled in a Kugelrohr distillation apparatus for 3 h. During the course of heating, 45 mg of a dark colored oil was distilled out and chromatographed (SiO_2, benzene) to give 20 mg (75%) of **14**, 10 mg (61%) of diphenyl disulfide, and 8 mg (17%) of **7**. The carboxylic acid **14** was esterified with CH_2N_2 and subjected to preparative GLC (SE-30) to show a single peak: IR ($CHCl_3$) 3400—2400 (OH), 1697 (C=O) cm^{-1}; NMR: δ 9.59 (s, 1, CO_2H), 6.94 (s, 2, ArH), 3.72 (s, 2, CH_2), 2.28 (s, 3, CH_3), 2.24 (s, 3, CH_3), 2.20 (s, 3, CH_3). Methyl ester of **14**; Found: C, 74.90; H, 8.55%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

References

1) Alicyclic Terpenoids from Cyclocitryl Phenyl Sulfides VIII. Part VII. S. Torii, K. Uneyama, I. Kawahara, and M. Kuyama, *Chem. Lett.*, **1978**, 455.

2) W. S. Johnson, *Acc. Chem. Res.*, **1**, 1 (1968); E. E. van Tamelen, *ibid.*, **1**, 111 (1968); T. Kato and S. Kumazawa, *Yuki-goseikagaku Kyokaishi*, **33**, 223 (1975); W. S. Johnson, *Angew. Chem. Int. Ed. Engl.*, **15**, 9 (1976).

3) The cyclization of homogeranic acid with $SnCl_4$ in nitromethane yielded 51% of *cis*-**9a**: a) T. Kato, S. Kumazawa, and Y. Kitahara, *Synthesis*, **1972**, 573; b) S. Kumazawa, T. Kato, and Y. Kitahara, *Chem. Lett.*, **1973**, 633.

4) a) S. Torii, K. Uneyama, and M. Ishihara, *Chem. Lett.*, **1975**, 479; b) K. Uneyama and S. Torii, *Tetrahedron Lett.*, **1976**, 443; c) K. Uneyama and S. Torii, *Chem. Lett.*, **1977**, 39; d) S. Torii, K. Uneyama, and H. Hamada, *Bull. Chem. Soc. Jpn.*, **50**, 2503 (1977).

5) S. Torii, K. Uneyama, and M. Kuyama, *Tetrahedron Lett.*, **1976**, 1513.

6) T. Sakan, S. Isoe, and S. B. Hyeon, *Tetrahedron Lett.*, **1967**, 1623.

7) a) W. C. Bailey, Jr., A. K. Bose, R. M. Ikeda, R. H. Newman, H. V. Secor, and C. Varsel, *J. Org. Chem.*, **33**, 2819 (1968); b) S. Fukushima, Y. Akahori, and T. Tsuneya, *Yakugaku Zasshi*, **88**, 646 (1968); c) H. Kaneko and K. Ijichi, *Agric. Biol. Chem.*, **32**, 1337 (1968); d) E. von Sydow and K. Anjou, *Lebensm. Wiss. Technol.*, **2**, 78 (1969); e) S. Fukushima, Y. Akahori, and T. Tsuneya, *Yakugaku Zasshi*, **89**, 1729 (1969); f) K. Ina, Y. Sakato, and H. Fukami, *Tetrahedron Lett.*, **1968**, 2777; g) T. Fujimori, R. Kasuga, H. Matsushima, H. Kaneko, and M. Noguchi, *Agric. Biol. Chem.*, **40**, 303 (1976).

8) H. Kaneko and K. Hoshino, *Agric. Biol. Chem.*, **33**, 969 (1969).

9) E. Demole and P. Enggist, *Helv. Chim. Acta*, **51**, 481 (1968).

10) E. A. Lehto and D. A. Shirley, *J. Org. Chem.*, **22**, 989 (1957).

11) a) M. Mousseron-Canet, J. C. Mani, and J. P. Dalle, *Bull. Soc. Chim. Fr.*, **1967**, 608; b) S. Isoe, S. B. Hyeon, H. Ichikawa, S. Katsumura, and T. Sakan, *Tetrahedron Lett.*, **1968**, 5561; c) K. Ina, T. Takano, Y. Imai, and Y. Sakato, *Agric. Biol. Chem.*, **36**, 1033 (1972); d) B. R. von Warburg, H. R. Wolf, and O. Jeger, *Helv. Chim. Acta*, **56**, 1948 (1973); e) S. Kurata, Y. Inouye, and H. Kakisawa, *Tetrahedron Lett.*, **1973**, 5153; f) S. Kurata, T. Kusumi, Y. Inouye, and H. Kakisawa, *J. Chem. Soc. Perkin Trans 1*, **1976**, 532.

12) a) S. Isoe, S. B. Hyeon, and T. Sakan, *Tetrahedron Lett.*, **1969**, 279; b) U. Schwieter, W. Arnold, W. E. Oberhänsli, N. Rigassi, and W. Vetter, *Helv. Chim. Acta*, **54**, 2447 (1971); c) S. Isoe, S. B. Hyeon, S. Katsumura, and T. Sakan, *Tetrahedron Lett.*, **1972**, 2517; d) K. Kawashima and T. Yamanishi, *Nippon Nogei Kagaku Kaishi*, **47**, 79 (1973).

13) D. Lerner, J. C. Mani, and M. Mousseron-Canet, *Bull. Soc. Chim. Fr.*, **1970**, 1968.

14) a) Ref. 6; b) Ref. 7a; c) Ref. 9; d) Z. Horii, M. Ito, I. Minami, M. Yamauchi, M. Hanaoka, and T. Monose, *Chem. Pharm. Bull.*, **18**, 1967 (1970); e) M. Stoll, P. Bolle, and L. Ruzicka, *Helv. Chim. Acta*, **33**, 1510 (1950); f) Ref. 16.

15) M. Robi and C. H. Engster, *Helv. Chim. Acta*, **52**, 1732 (1969).

16) T. Matsumoto, G. Sakata, Y. Tachibana, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 1147 (1972).