The Synthesis of Cubebol from (−)-Carvone by Introducing the Electrochemical Acetoxylation Reaction

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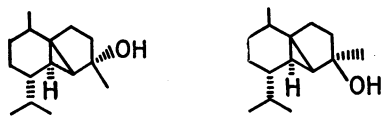
The synthesis of cubebol and the related compounds from (−)-carvone is described. In the preparation of the key intermediate, 7,10-*trans*-2,6-epi-2-acetoxy-7-isopropyl-10-methyltricyclo[4.4.0.0^{1,5}]decan-4-one (**10**) the electrochemical acetoxylation reaction could be used as an effective method for introducing the acetoxy group at C-2 carbon atom instead of the carboxy function of 7,10-*trans*-2,6-epi-4-oxo-7-isopropenyl-10-methyltricyclo-[4.4.0.0^{1,5}]decan-2-carboxylic acid (**6a**). The condensation of (+)-*p*-menth-8-en-2-one (**2a**) prepared from (−)-carvone with dimethyl succinate afforded Stobbe half-ester **3**, which provided the diazoketone **4** smoothly. Thermal decomposition of **4** in benzene gave intramolecular adducts **5a** and **5b** (4: 1). Hydrolysis of **5a** afforded **6a** in *ca.* 40% yield. Electrolysis of **6a** in AcOH–*t*-BuOH–Et_3N (2: 1: 0.1) using platinum electrodes gave **10** in 72% yield. Elimination of acetic acid gave two isomers **11a** and **11b** (3: 1) in 87% yield and subsequent methylation of **11a** afforded 7-isopropyl-4,10-dimethyltricyclo[4.4.0.0^{1,5}]deca-2-en-4-ol (**12**) in 82% yield, which on hydrogenation gave the desired product **1a** (36.5%) along with the epimer **1b** (36.5%).

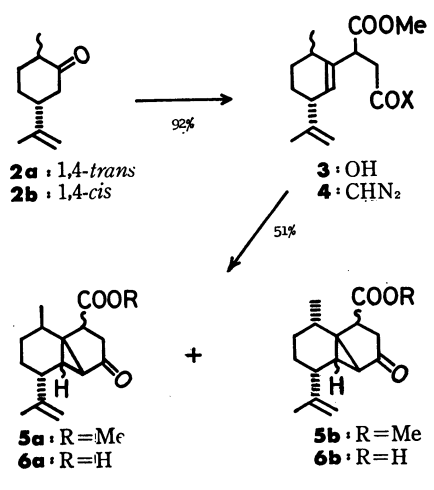
For the synthesis of complex sesquiterpenes, principal components in essential oils, cubebol (**1a**) and its related compounds, α- and β-cubebenes, isolated from the essential oil of the fruits of cubeb (*Piper cubeba* L.)[1] and citrus oils[2] are of interest as regards their synthesis.



1a **1b**

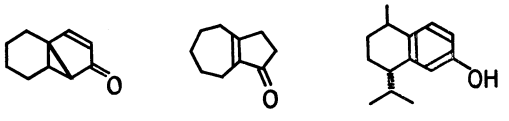
Recently, Yoshikoshi *et al.*,[1c] reported the preparation of **1a**, elucidating the stereochemistry of the related sesquiterpenoids. The present work deals with a convenient synthesis of **1a** from (−)-carvone by means of an electrochemical method. An electrochemical procedure for the replacement of carboxyl function to acetoxy group at the C-2 carbon atom of tricyclo[4.4.0.0^{1,5}]-decan-4-one system was reported.[3] In order to utilize electrochemical acetoxylation in cubebol synthesis it is desirable to find an intermediate which is easily prepared and stable during the course of electrolysis. We chose 7,10-*trans*-2,6-epi-7-isopropenyl-10-methyl-4-oxotricyclo[4.4.0.0^{1,5}]decan-2-carboxylic acid (**6a**) for the present synthesis.

The Stobbe condensation of (+)-8-*p*-methen-2-one (**2a**), contaminated with 24% of 8-*p*-isomenthen-2-one (**2b**),[4] with dimethyl succinate afforded the starting material **3** in 92% yield. In order to obtain the tricyclo[4.4.0.0^{1,5}]decan-4-one skeleton, intramolecular addition of keto-carbene to the double bond of **3** was attempted.[5] The diazoketone **4** obtained by the reaction of acid chloride of **3** with diazomethane was subjected to thermal decomposition in benzene at 80—81 °C using bis(*N*-propylsalicylideneaminato)copper(II) as a soluble catalyst.[6] This afforded 51% yield (based on **3**) of a C-10 isomeric mixture of the adducts **5a** and **5b**, which was separated by column chromatography over alumina to afford 40% of **5a** and 11% of **5b**. Hydrolysis of **5a** in 5% aqueous methanolic potassium hydroxide afforded **6a** quantitatively.



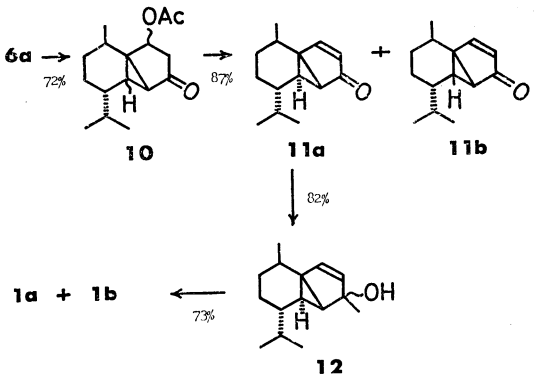
2a : 1,4-*trans*
2b : 1,4-*cis*
3 : OH
4 : CHN_2
5a : R=Me
6a : R=H
5b : R=Me
6b : R=H

Mc Murry and Blaszczak[7] reported a new method for the synthesis of the cyclic enones from β-carboxy ketones by oxidative decarboxylation with lead tetraacetate in the presence of cupric ion. However, the method could only be applied to γ-methyl-β-carboxy ketones. It seems that application of stepwise reactions and mild reaction conditions is particularly suitable for the complex acid **6a**. We have encountered some difficulties in obtaining the enones **7** selectively from

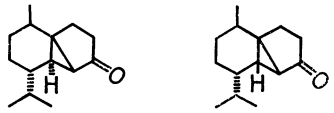


7 **8** **9**

4-oxotricyclo[4.4.0.0^{1,5}]decan-2-carboxylic acid by electrolytic decarboxylation directly, a mixture of **7** and **8** being obtained.[3] Under similar electrolysis conditions, the acid **6a** afforded a mixture of the enone **11** and the aromatic compound **9**. The synthesis of the enone **11** was successfully accomplished on treatment of the acetate **10** with triphenylmethylenephosphorane.[8] Thus, electrolytic acetoxylation of **6a** in a mixed solvent of acetic acid-*t*-butyl alcohol-trimethylamine (2:1:0.1) using platinum electrodes with a constant current of 0.08 A/cm^2, applied voltage *ca.* 20 V (1.6—1.7 *vs.* SCE) at 10 °C for 20 h afforded 72% of the acetate **10** as the sole product.[3] Under these electrolytic conditions,



hydrogenation to the isopropenyl function of **6a** occurred spontaneously. The conversion of **10** into an epimeric mixture of α,β-unsaturated ketones **11a** and **11b** (3: 1) was accomplished in 87% yield on treatment with a benzene solution containing a slightly excess amount of triphenylmethylenephosphorane at 0—4 °C. Separation of the epimers **11a** and **11b** was carried out by preparative glpc to afford the desired **11a** in 65% yield (based on **10**). The Grignard reaction of **11a** with methyl magnesium iodide resulted in the formation of C-4 isomeric mixtures **12** in 82% yield. Without separation of the isomers, **12** was hydrogenated over platinum oxide to afford cubebols **1a** and **1b** (1: 1) in 73% yield. Separation of the isomers could be achieved by column chromatography over silica gel.



13a **13b**

Norcubebanone **13a**[9] prepared from hydrogenation of **11a** could be used for the preparation of **1a** by the reaction with methylmagnesium iodide.[1c] The coupling of alkylmetals with the carbonyl group of the bicyclo[3.1.0]hexan-2-ones occurred mainly on the side opposite the cyclopropane ring.[1c,10] However, the Grignard reactions of **11a** and/or **13a** with methyl magnesium iodide provided a small amount of the epimer **1b** together with **1a**.

Experimental

Melting points and boiling points are uncorrected. NMR spectra were determined with a Hitachi R-24 instrument. IR spectra were recorded on a Hitachi EPI-S2, only the major absorptions being cited. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer at 70 eV, the molecular and major fragment ions being cited: *m/e* (relative intensity).

Electrolysis Apparatus. The electrolytic vessel was a water-jacketed beaker, diam. 2.5 cm, height 10 cm, fitted with a gas lead pipe, thermometer and magnetic stirrer, two smooth platinum electrodes (3 cm^2) being placed parallel to each other 3 mm apart. The current was controlled by adjusting the voltage. The direction of current was changed every 30 s by means of a commutator.

Preparation of Stobbe Half-ester (3). A solution of (+)-8-*p*-menthen-2-one (**2**), $[\alpha]_D^{14}$ +18.8° (*c* 3.03, $CHCl_3$)[4] (500 mg, 3.3 mmol) and dimethyl succinate (720 mg, 4.9 mmol) was treated with *t*-BuOK (from 200 mg of K metal) in 5 ml of dry *t*-BuOH. The mixture was heated at *ca.* 90 °C for 3 h with stirring. After being cooled to 0 °C the mixture was acidified with ice-cold 10% HCl. The organic phase was extracted with ether–benzene (1: 1). The extracts were washed with water, dried (Na_2SO_4), and concentrated. The residue (920 mg) was chromatographed over silica gel. Elution with 70 ml of hexane–ether (9: 1, monitored by TLC) gave a fraction of R_f 0.26—0.62. Subsequent elution with *ca.* 60 ml of acetone gave 805 mg (92%) of **3** (R_f 0.19): IR (neat) 3400—2500 (COOH), 1740 (ester), 1715 (COOH), 1645 (C=C), and 892 cm^{-1}; NMR ($CDCl_3$) δ 0.95—1.14 (m, 3H, CH_3), 1.68 (s, 3H, CH_3C=C), 3.64 (s, 3H, CH_3O), 4.45—4.80 (m, 2H, H_2C=C), and 5.41 (m, 1H, HC=C); $[\alpha]_D^{13}$ +54.75° (*c* 2.56, $CHCl_3$).

Found: C, 67.48; H, 8.29%. Calcd for $C_{15}H_{22}O_4$: C, 67.65; H, 8.33%.

2,6,10-Epi-2-methoxycarbonyl-7-isopropenyl-10-methyltricyclo[4.4.0.0^{1,5}]decan-4-ones (5a and 5b). To a stirred suspension of 72 mg of NaH (50% mineral oil dispersion, washed with anhydrous hexane before use) in 10 ml of dry benzene, was added dropwise 266 mg (1 mmol) of **3** in 3 ml of dry benzene. The mixture was stirred for 1 h at room temperature and 0.2 ml of oxalyl chloride was added at 5 °C. Stirring was continued for 1 h at room temperature and the mixture was filtered under N_2. The residual acid chloride was dissolved in 2 ml of dry benzene. The benzene solution was treated with excess diazomethane at 0 °C. The mixture was stirred overnight at 0—5 °C. Removal of the solvent under reduced pressure at 10 °C and subsequent chromatography over alumina with CH_2Cl_2 gave 210 mg of the diazo ketone **4**, a yellow oil: IR (neat) 2075 (CN_2), 1737 (ester), and 1645 cm^{-1} (diazo ketone); NMR ($CDCl_3$) δ 0.95—1.18 (m, 3H, CH_3), 1.67 (s, 3H, CH_3C=C), 3.43 (s, 3H, CH_3O), 4.45—4.80 (broad d, 2H, H_2C=C), 5.20 (s, 1H, $COCHN_2$), and 5.38 (m, 1H, HC=C). Without further purification, the diazo ketone (210 mg, 0.72 mmol) was added to a mixture of 40 ml of benzene and 20 ml of bis(*N*-propylsalicylideneaminato)-copper(II), dried in an oven at 80—100 °C for 10 min before use, and dissolved in 5 ml of dry benzene with vigorous stirring at 80—81 °C for 4 hr. The solvent was then removed on a rotoevaporator and the residue was chromatographed over alumina. Elution with 20 ml of hexane–ether (2: 1, monitored by tlc) gave 105 mg (40%) of **5a** (R_f 0.77) and subsequent elution with 20 ml of hexane–ether (1: 1) gave 29.1 mg (11%) of **5b** (R_f 0.53). The spectral data along with elemental analyses are as follows: *7,10-trans-2,6-epi-2-methoxycarbonyl-7-isopropenyl-10-methyltricyclo[4.4.0.0^{1,5}]decan-4-one (5a)*: IR (neat) 3080, 1732 (C=O), and 1648 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.95—1.18 (m, 3H, CH_3), 1.75 (s, 3H, CH_3C=C), 3.72 (s, 3H, CH_3O), and 4.86 (broad, 2H, H_2C=C); mass spectrum (*m/e*) 262 (M^+, 14), 247 (14), 234 (15), 203 (22), 181 (21), 175 (20), 161 (25), 159 (29), 147 (39), and 135 (100); $[\alpha]_D^{24}$ +6.1° (*c* 3.68, $CHCl_3$).

Found: C, 73.13; H, 8.51%. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%.

7,10-cis-2,6-Epi-2-methoxycarbonyl-7-isopropenyl-10-methyltricyclo[4.4.0.0^{1,5}]decan-4-one (5b): IR (neat) 3080, 1737 (C=O), and 1647 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.47—1.18 (m, 3H, CH_3), 1.78 (broad, 3H, CH_3C=C), 3.66 (s, 3H, CH_3O), and 4.75 (m, 2H, H_2C=C); mass spectrum (*m/e*) 262 (M^+, 9), 247 (13), 234 (8), 203 (26), 181 (13), 175 (19), 161 (26), 159 (22), 147 (44), and 135 (100); $[\alpha]_D^{24}$ −8.5° (*c* 2.64, $CHCl_3$).

Found: C, 73.08; H, 8.60%. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%.

7,10-trans-2,6-Epi-7-isopropenyl-10-methyl-4-oxotricyclo[4.4.0.0^{1,5}]decene-2-carboxylic Acid (6a). A mixture of

330 mg (1.26 mmol) of **5a** and 700 mg (12.5 mmol) of KOH in 20 ml of 5% aqueous MeOH was stirred at room temperature overnight. The solvent was removed on a rotoevaporator. The residual alkaline solution was washed with hexane–benzene and neutralized with aqueous tartaric acid under cooling with an ice-water bath and then extracted with ether. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The residue (312 mg) was chromatographed over silica gel using hexane–ether (1: 1) to give 305 mg (98%) of **6a**: IR (neat) 3500—2500 (COOH), 1728 (C=O), 1705 (COOH), and 1645 cm^{-1}; NMR ($CDCl_3$) δ 1.02—1.19 (d, J=6.5 Hz, 3H, CH_3), 1.74 (s, 3H, CH_3C=C), 3.15—3.60 (m, 1H, HCC=O), 4.73 (broad, 2H, H_2C=C), and 10.63 (broad, 1H, COOH); $[\alpha]_D^{24}$ +7.7° (*c* 2.92, $CHCl_3$).

Found: C, 72.44; H, 8.38%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

Electrolytic Acetoxylation of 6a. The acid **6a** (150 mg, 0.61 mmol) was dissolved in a mixed solution of AcOH (6 ml), *t*-BuOH (3 ml), and Et_3N (20 mg). The mixture was electrolyzed at a constant current of *ca.* 0.25 A (*ca.* 20 V) at 10 °C for 20 h. The solvent was removed on a rotoevaporator and the residue was taken up in benzene–ether (1: 1). The organic phase was washed with water and saturated $NaHCO_3$ and dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel using hexane–ether (2: 1) to give 115 mg (72%) of **10**, bp 129—130 °C (0.005 mmHg).[3]

7,10-trans-*6-Epi-7-isopropyl-10-methyltricyclo*[*4.4.0.0*^{1,5}]-2-*decen-4-ones (11a and 11b).* A salt free benzene solution (10 ml) of triphenylmethylenephosphorane prepared from triphenylmethylphosphonium bromide (210 mg, 0.59 mmol) was added dropwise with cooling in an ice–water bath to a stirred solution of **10** (119 mg, 0.45 mmol) in 2 ml of benzene. The mixture was diluted with 20 ml of hexane and the precipitate was filtered off. The filtrate was concentrated. The residual oil was chromatographed over silica gel tlc plate (Merck PF-254, hexane–ether, 1: 1) to give 80 mg (87%) of **11a** and **11b** (R_t 0.64—0.72). Separation of the epimers was carried out by preparative glpc to give **11a** and **11b** in a 3: 1 ratio (polyneopentyl glycol succinate, 10% coated on Chromosorb W, 4 mm×2 m column, carrier gas H_2 32 ml/min, 169 °C, R_t (min) **11a** (11.00), **11b** (15.00).

6,7-cis-*7,10*-trans-*7-Isopropyl-10-methyltricyclo*[*4.4.0.0*^{1,5}]-2-*decen-4-one (11a)*: IR (neat) 3020, 1702 (C=O), and 1571 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.60—1.07 (10H, $3CH_3$, CH), 1.10—2.40 (m, 8H, CH_2, CH), 5.55 (d, J=9 Hz, 1H, CH=C), and 7.46 (d, J=9 Hz, 1H, HC=C); mass spectrum (*m/e*) 204 (M^+, 39), 189 (50), 161 (100), 149 (56), 148(53), 147 (57), 133 (84), 121 (50), 109 (62), 105 (75), and 91 (94); $[\alpha]_D^{24}$ −136.7° (*c* 1.88, $CHCl_3$).

Found: C, 82.15; H, 10.02%. Calcd for $C_{14}H_{20}O$; C, 82.30; H, 9.87%.

6,7-trans-*7,10*-trans-*7-Isopropyl-10-methyltricyclo*[*4.4.0.0*^{1,5}]-*decene-4-one (11b)*: IR (neat) 3080, 1706 (C=O), and 1568 cm^{-1} (C=C); NMR ($CDCl_3$) δ 0.60—1.10 (10H), 1.10—2.40 (8H), 5.48 (d, J=9 Hz, 1H, HC=C), and 7.62 (d, J=9 Hz, 1H, HC=C); mass spectrum (*m/e*) 204 (M^+, 39), 189 (38), 161 (83), 149 (54), 148 (25), 147 (48), 133 (56), 121 (46), 109 (34), 105 (58), and 91 (100); $[\alpha]_D^{24}$ +77.4° (*c* 0.23, $CHCl_3$).

Found: C, 82.26; H, 9.82%. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87%.

7-Isopropyl-4,10-dimethyltricyclo[*4.4.0.0*^{1,5}]*deca-2-en-4-ol (12).* A solution of **11a** (26 mg, 0.13 mmol) in ether (3 ml) was added for 10 min to a stirred solution of MeMgI prepared from MeI (50 mg, 0.35 mmol) and Mg metal (5 mg, 0.21 mg atom) under N_2 and cooling with ice. The solution was gently refluxed for 2 h. After being cooled to room temperature the mixture was poured into aqueous 20% NH_4Cl (5 ml) and extracted with benzene. The extracts were washed with water, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed over silica gel with benzene to give **12** (23.0 mg, 82%): IR (neat) 3400 (OH), 3050 (shoulder), 1370, 1027, 917, and 756 cm^{-1}; NMR (CCl_4) δ 0.60—1.20 (m, 14H, $3CH_3$, CH_2, CH), 1.40 (d, 3H, CH_3), 1.40—1.80 (m, 5H, CH_2, CH), 5.00—5.24 (m, 1H, HC=C), and 5.52—5.76 (m, 1H, HC=C); mass spectrum (*m/e*) 220 (M^+, 7), 207 (32), 202 (28), 177 (56), 161 (53), 159 (78), 145 (29), 135 (43), 131 (58), 121 (58), 119 (57), 118 (100), 117 (58), 105 (63); $[\alpha]_D^{24}$ −91.5° (*c* 0.87, $CHCl_3$).

Found: C, 81.50; H, 11.04%. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98%.

Hydrogenation of 12. To a solution of **12** (34.0 mg, 0.15 mmol) in 5 ml of AcOEt was added 5 mg of platinum dioxide. The mixture was flushed with H_2 gas and stirred efficiently under H_2. After 1 h the theoretical amount of H_2 was absorbed. The mixture was filtered and the solvent was rotoevaporated to afford a residue which was immediately chromatographed over silica gel (2.5 g). Careful elution with benzene gave 4-epicubebol (**1b**, 12.5 mg, 36.5%) as an oil contaminated with a small amount of **1a**. The following elution with benzene gave cubebol (**1a**) (12.5 mg, 36.5%) as crystals. Repeated chromatography of the products over silica gel using benzene gave analytical samples: cubebol (**1a**), mp 58—59 °C (lit,[1a,1c] 61—62 °C, 64 °C); IR (Nujol) 3300 (OH), 1385, 1370, 1300, 1223, 1155, 1134, 1080, 1032, 980, 970, 928, and 890 cm^{-1}; NMR ($CDCl_3$) δ 0.89 (d, J=7 Hz, 6H, CH_3), 0.95 (d, J=6.5 Hz, 3H, CH_3), and 1.27 (s, 3H, CH_3); mass spectrum (*m/e*) 222 (M^+,2), 207 (39), 204 (29), 189 (4), 179 (8), 161 (100), 121 (32), 119 (58), 105 (72), and 91 (55); $[\alpha]_D^{15}$ −44.7° (*c* 0.85, $CHCl_3$) (lit,[1c,1a] −48.3 °, −61.6 °).

4-Epicubebol (1b): IR (neat) 3400 (OH), 1370, 1321, 1152, 1123, 1040, 1008, 980, and 915 cm^{-1}; NMR (CCl_4) δ 0.87—1.05 (m, $3CH_3$), and 1.25 (s, 3H, CH_3); mass spectrum (*m/e*) 222 (M^+, 3), 207 (53), 204 (26), 189 (6), 179 (21), 161 (100), 121 (54), 120 (55), 119 (58), 105 (67), and 91 (64); $[\alpha]_D^{14}$ −4.0° (*c* 1.25, $CHCl_3$).

7,10-trans-*7-Isopropyl-10-methyltricyclo*[*4.4.0.0*^{1,5}]*decan-4-one (norcubenbanone) (13a).* Hydrogenation of 44 mg (0.22 mmol) of **11a** was carried out in 3 ml of absolute EtOH with 40 mg of 10% Pd–carbon until 4.8 ml of H_2 gas was absorbed. The mixture was filtered and the solvent was evaporated to afford an oil. The crude product was chromatographed on silica gel, eluted with benzene, to give 44 mg (99%) of **13a**, mp 57.0—57.5 °C (lit,[1c] mp 57—58 °C); mass spectrum (*m/e*) 206 (M^+, 42), 191 (10), 164 (78), 163 (45), 149 (32), 134 (31), 122 (100), 93 (77), and 79 (92); $[\alpha]_D^{24}$ −22.8 ° (*c* 0.12, MeOH). (lit,[1c] $[\alpha]_D^{24}$ −23.9° (*c* 0.16, MeOH)). IR and NMR spectra of **11a** were identical with those of an authentic sample.[9]

Cubebol (1a) from Norcubebanone (13a). To an ether solution of MeMgI, prepared from MeI (80 mg, 0.56 mmol) and Mg metal (10 mg, 0.42 mg atom), was added 33 mg (0.16 mmol) of **13a** in 5 ml of ether over a period of 5 min. The stirred mixture was refluxed for 2 h and poured into ice-cold aqueous 20% NH_4Cl (5 ml). The organic phase was extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel using benzene to give **1a** (17.3 mg, 49%). Compound **1a** melted at 58—59 °C. IR and NMR spectral data were identical with those of an authentic sample.

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