Synthesis of 7-Alkylidene-5-oxadispiro[2.0.4.4]dodecan-6-ones

Kiyomi KAKIUCHI,* Takehito YONEI, Yoshito TOBE, and Yoshinobu ODAIRA
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
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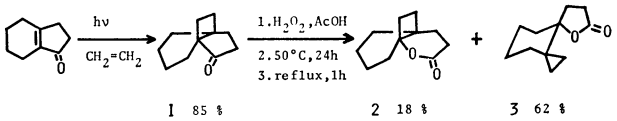
7-Alkylidene-5-oxadispiro[2.0.4.4]dodecan-6-ones, having a cyclopropane ring, were synthesized by the α-alkylidenation of easily available 5-oxadispiro[2.0.4.4]dodecan-6-one. Also, α-alkylidene-γ-butyrolactones, containing an additional hydroxyl group, were prepared. The screening of the biological activities of these γ-lactones gave the interesting results. For instance, α-isopropylidene-γ-lactone exhibited the antiarrhythmia activity *in vivo*.

Recently, α-methylene-γ-butyrolactones have been the subject of extensive research because a large number of sesquiterpene lactones, containing α-methylene-γ-butyrolactone moiety, have been shown to exhibit marked antitumor, cytotoxic, and other biological activities attributed to this moiety.[1a,b] The biological activities of these lactones are apparently driven from significant chemical affinity of this moiety for the thiol groups of sulfhydryl enzymes.[1c-f] In particular, interest in α-methylene-γ-butyrolactones as medical agents has been stimulated by the possibility that some of these might show enough selective toxicity against neoplastic cells to be of the therapeutic value as anticancer agents.[1b,c,g] Although the enone component is essential for the biological activities, there are additional factors which may enhance these properties. These enhancement factors include the presence of some substituents such as hydroxyl group or epoxy ring which may facilitate the addition of sulfide anion or proton transfer at some intermediate stage in the addition involving the thiol groups of enzymes.[1a,h] On the other hand, it has been well known that some natural products, having a cyclopropane ring, display remarkable biological activities.[2] For example, illudin S, containing a spiro cyclopropane ring, is well examined about antitumor activity.[2b] Previously, we reported on the synthesis of 5-oxadispiro-[2.0.4.4]dodecan-6-one (**3**) (γ-lactone), containing a spiro cyclopropane ring, by the acid catalyzed or thermally induced cyclobutyl-cyclopropylcarbinyl rearrangement of 2-oxatricyclo[4.4.2.0^{1,6}]dodecan-3-one (**2**) (δ-lactone).[3] From the above point of view, the γ-lactone **3** may be advantageously taken as a useful intermediate for the synthesis of a new type of α-alkylidene-γ-butyrolactones. As part of the studies on the structure-biochemical activity relationship,[4] we wish to describe here the synthesis of several 7-alkylidene-5-oxadispiro[2.0.4.4]dodecan-6-ones (**4a**—**h**) from the γ-lactone **3** and the interesting results on the screening of the biological activities of the α-alkylidene-γ-lactones *in vivo*.

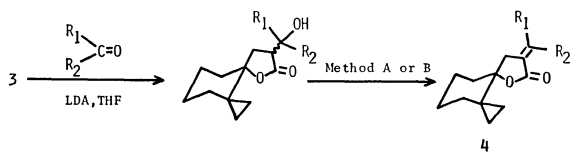
Results and Discussion

Propellalactone **2** was prepared by the Baeyer-Villiger oxidation of tricyclo[4.3.2.0^{1,6}]undecan-7-one (**1**), easily derived from the photocycloaddition of bicyclo[4.3.0]non-1(6)-en-7-one to ethylene as described previously.[6] In practice, however, the reaction mixture after the above oxidation without isolation of propellalactone **2** was heated at 50 °C for 1 d and then refluxed gently for 1 h to give a 78:22 ratio of dispiro-γ-lactone **3** and propellalactone **2** in 80% yield. The γ-lactone **3** was readily isolated from the reaction mixture by column chromatography on silica gel (Scheme 1).



Scheme 1.

α-Alkylidenation of the γ-lactone **3** was carried out according to the usual method[7] comprised of α-hydroxyalkylation and subsequent dehydration as shown in Scheme 2. To a solution of lithium diisopropylamide (LDA) in anhydrous tetrahydrofuran (THF) at −78 °C was slowly added a solution of the γ-lactone **3** in anhydrous THF and hexamethylphosphoric triamide (HMPT). After stirring at −78 °C for 30 min, the carbonyl compound was added and the mixture was stirred for 2 h. In the case of α-hydroxymethylation, gaseous formaldehyde was passed into the reaction mixture at −20 °C under nitrogen stream. In every case, α-hydroxyalkylation proceeded smoothly to afford the desired products in 80—100% yields. The crude products of α-hydroxyalkyl-γ-lactones were subjected to the next reaction without isolation. Next, the dehydration of the α-hydroxyalkyl-γ-lactones was carried out by means of two methods, depending upon the type of the hydroxyl group. Namely, when the hydroxyl group was primary or secondary, a solution of the alcohol in dry pyridine was treated with methanesulfonyl (Ms) chloride at 5 °C for 9 h, and the obtainable mesylate was dissolved in dry benzene containing 1.4 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and then stirred at room temperature for 6 h (method A).[7b] On the other hand, when the hydroxyl group was tertiary, thionyl chloride was added to a solution of the alcohol in dry pyridine and dry dichloromethane and the reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 4 h (method B).[8] After usual work-up, the crude product of 7-alkylidene-5-oxadispiro[2.0.4.4]dodecan-6-ones (**4a**—**f**) was obtained and purified by column chromatography on silica gel. The use of aldehydes as the carbonyl compound in the α-hydroxyalkylation resulted in the formation of *E*/*Z* stereoisomers of the γ-lactones (**4b**—**e**). They were, however, separated successfully by the careful chromatography. The results are summarized in Table 1.



Method A: 1. MsCl, Pyridine, 2. DBU, PhH.
Method B: $SOCl_2$, Pyridine, CH_2Cl_2.

Scheme 2.

Table 1. Synthesis of α-alkylidene-γ-butyrolactones

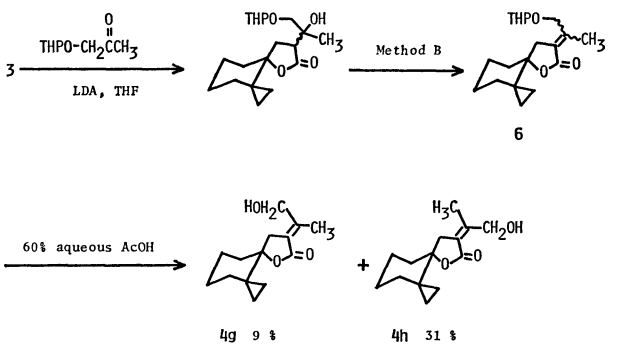
Carbonyl compd	α-Alkylidene-γ-butyrolactone	R_1	R_2		Yield/%[a]
Formaldehyde	**4a**	H	H		77[b]
Acetaldehyde	**4b**	CH_3	H	(*E*)	54
	4c	H	CH_3	(*Z*)	7
Propionaldehyde	**4d**	C_2H_5	H	(*E*)	30
	4e	H	C_2H_5	(*Z*)	20
Acetone	**4f**	CH_3	CH_3		52

a) Isolated yield based on **3**. b) Determined by ^1H NMR analysis.

It was easy to establish the stereochemistry around the olefinic part of the γ-lactones **4b**—**e** by the comparison of the ^1H NMR chemical shifts of the vinyl protons of **4b**—**e** with those of α-alkylidene-γ-butyrolactones described in literature.[9] The chemical shifts of the olefinic protons (6.57 and 6.11 ppm for *E* and *Z* isomers, respectively) were the most remarkable point to descriminate between the geometrical isomers of α-ethylidene-γ-lactones (**4b**) and (**4c**). Similarly, the observed values of the olefinic protons (6.48 and 6.00 ppm) of α-propylidene-γ-lactones (**4d**) and (**4e**) distinguished one from the other.

Furthermore, we tried to synthesize the α-alkylidene-γ-lactones having a hydroxyl group which was expected to enhance the reactivity of the conjugated lactone toward biological nucleophiles as mentioned earlier. The tetrahydropyran-2-yl (THP) ether of hydroxyacetone (**5**) was used for α-hydroxyalkylation of the γ-lactone **3**. Dehydration by the method B gave the mixture of *E*/*Z* isomers of the THP–ether (**6**), which was treated with 60% aqueous acetic acid at 45 °C for 3 h. After usual work-up followed by purification by column chromatography on silica gel, (*E*)- and (*Z*)-α-(2-hydroxy-1-methylethylidene)-γ-lactones (**4g**) and (**4h**) were obtained in 9% and 31% overall yields from the γ-lactone **3**, respectively (Scheme 3). The distinction in stereochemistry between two isomers was accomplished by the comparison of the chemical shifts of the methyl groups in ^1H NMR spectra (2.16 and 1.90 ppm for *E* and *Z* isomers, respectively) with those of α-isopropylidene-γ-lactone (**4f**), since the methyl groups of **4f** located in *syn*- and *anti*-positions toward the carbonyl group show resonances at 2.20 and 1.84 ppm, respectively.

The screening of biological activities of a series of the present α-alkylidene-γ-butyrolactones **4a**, **4b**, **4d**—**f**, and **4h** gave attractive results. Concerning the antitumor activity of these γ-lactones against Sarcoma 180 A *in vivo*, all of them were less active than the famous antitumor antibiotic, Mitomycin C. Interestingly, the other biological activities of these γ-lactones *in vivo*, however, were found out: the antihistamine activity of (*E*)-α-propylidene-γ-lactone **4d**, the antihistamine and the anticholine activities of (*Z*)-α-propylidene-γ-lactone **4e**, the antiarrhythmia activity of α-isopropylidene-γ-lactone **4f**, and the platelet aggregation inhibition activity of (*Z*)-α-(2-hydroxy-1-methylethylidene)-γ-lactone **4h**.



Scheme 3.

In this way, 7-alkylidene-5-oxadispiro[2.0.4.4]dodecan-7-ones **4a**—**h**, having a spiro cyclopropane ring, were synthesized and the interesting results relating to the biological activities of these lactones were given.

Experimental

All melting and boiling points are uncorrected. IR spectra were recorded with a JASCO IR-G spectrometer as liquid film unless otherwise stated. ^1H NMR spectra were obtained on a JEOL JNM-PS-100 instrument using Me_4Si as an internal standard and CCl_4 as a solvent. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph and preparative GLC separation was conducted on a Varian Aerograph 920 gas chromatograph.

Acetaldehyde, propionaldehyde, and hydroxyacetone were distilled prior to use. Acetone was distilled from potassium carbonate before use. Tricyclo[4.3.2.$0^{1,6}$]undecan-7-one (**1**) was prepared in 85% yield by the photocycloaddition of bicyclo[4.3.0]non-1(6)-en-7-one[10] to ethylene in ether (0.4 M†) at −70 °C as described previously.[6]

5-Oxadispiro[2.0.4.4]dodecan-6-one (3). To a solution of 40.7 g (0.248 mol) of **1** in 500 ml of acetic acid was added 20-fold excess of 30% aqueous hydrogen peroxide. The mixture was stirred at room temperature for 7 d and at 50 °C for 1 d, then at gentle reflux for 1 h. The solution was poured into water and extracted with ether. The ethereal extracts were washed with saturated sodium carbonate (Na_2CO_3) solution, brine, and dried over anhydrous sodium sulfate (Na_2SO_4). The solvent was evaporated *in vacuo* to give 35.7 g of 2-oxatricyclo[4.4.2.$0^{1,6}$]dodecan-3-one (**2**) and γ-lactone **3** in a ratio 22:78 (by GLC analysis) (80%). The γ-lactone **3** was isolated by column chromatography (SiO_2, 8% ether–petroleum ether). Spectral and analytical data were already described.[3b]

General Procedure for Synthesis of α-Alkylidene-γ-butyrolactones (4a—f). *α-Hydroxyalkylation*: A solution of diisopropylamine (2 mmol) in dry THF (1.5 ml) cooled to −78 °C was treated dropwise with butyllithium (1.5 mmol) in hexane under nitrogen atmosphere. After stirring at −78 °C for 1 h, a solution of the γ-lactone **3** (1 mmol) in dry THF (0.2 ml) and dry HMPT (0.1 ml) was added dropwise *via* a

† 1 M = 1 mol dm^{-3}.

syringe. After addition was complete, stirring was continued at −78 °C for 30 min, then a carbonyl compound (1 mmol) was added *via* a syringe and the mixture was stirred for 2 h. The reaction was quenched by saturated ammonium chloride solution and the mixture was extracted with ether. The organic extracts were washed with 5% HCl, saturated sodium hydrogencarbonate ($NaHCO_3$) solution, brine, and dried (Na_2SO_4). The solvent was removed *in vacuo* to give the crude alcohol product.

Dehydration: *Method A.* The above alcohol (1 mmol) was dissolved in dry pyridine (2 ml) and treated at 0—5 °C with methanesulfonyl chloride (3 mmol). After stirring at 5 °C for 9 h, an ice-water was added and the mixture was extracted with ether. The ethereal extracts were washed with 5% HCl, saturated $NaHCO_3$ solution, and brine. After drying (Na_2SO_4), the solvent was evaporated under reduced pressure to give the crude mesylate. The crude mesylate (1 mmol) was dissolved in dry benzene (2.0 ml) containing DBU (1.4 mmol) and the mixture was stirred at room temperature for 6 h. Water was added and the product was extracted with ether. The organic layer was washed with 5% HCl, saturated $NaHCO_3$ solution, and brine. After drying (Na_2SO_4), the solvent was removed *in vacuo* leaving the crude α-alkylidene-γ-lactones.

Method B. Thionyl chloride (1.2 mmol) was added dropwise to a solution of the crude alcohol (1 mmol) in dry pyridine (0.5 ml) and dry CH_2Cl_2 (1.5 ml). The reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 4 h. After addition of a few pieces of ice, the mixture was extracted with CH_2Cl_2. The extracts were washed with 5% HCl, water, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give the crude α-alkylidene-γ-lactones. Analytical samples of the γ-lactones were obtained by preparative GLC.

*7-Methylene-5-oxadispiro[2.0.4.4]dodecan-6-one (**4a**).* The reaction of **3** (829 mg, 4.6 mmol) and formaldehyde, generated by depolymerization of paraformaldehyde (3.5 g) at 160 °C (bath temperature) and passed into the reaction mixture at −20 °C under nitrogen stream, gave the crude α-hydroxymethyl-γ-lactone (873 mg, 90%: IR 3450, 1750 cm^{-1}). Dehydration of the alcohol by method A (the mesylate: IR 1750, 1350, 1160 cm^{-1}) gave α-methylene-γ-lactone **4a** (684 mg). Overall yield based on **3** was 77% (determined by ^1H NMR analysis). **4a**: IR 3050, 1750, 1660 cm^{-1}; NMR δ 0.10—1.00 (m, 4H), 1.23—2.00 (m, 8H), 2.68 (t, J=2.8 Hz, 2H), 5.50 (t, J=2.6 Hz, 1H), 6.10 (t, J=2.6 Hz, 1H); MS *m/e* 192 (M^+). Found: C, 74.59; H, 8.56%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

*(E)- and (Z)-7-Ethylidene-5-oxadispiro[2.0.4.4]dodecan-6-one (**4b**) and (**4c**).* The reaction of **3** (5.7 g, 31.6 mmol) and acetaldehyde (1.4 g, 31.6 mmol) gave the crude α-(1-hydroxyethyl)-γ-lactone (7.3 g, quantitatively: IR 3450, 1740 cm^{-1}). Dehydration of the alcohol by method A (the mesylate: IR 1750, 1350, 1160 cm^{-1}) gave the mixture of *E*-isomer **4b** and *Z*-isomer **4c** which were separated by column chromatography (SiO_2, 3% ether–petroleum ether). **4b** (54% from **3**): IR 3050, 1750, 1670 cm^{-1}; NMR δ 0.10—1.00 (m, 4H), 1.12—2.04 (m, 11H), 2.55 (m, 2H), 6.57 (m, 1H); MS *m/e* 206 (M^+). Found: C, 75.43; H, 8.76%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. **4c** (7% from **3**): IR 3050, 1740, 1660 cm^{-1}; NMR δ 0.10—1.00 (m, 4H), 1.12—2.00 (m, 8H), 2.10 (m, 3H), 2.62 (m, 2H), 6.11 (m, 1H); MS *m/e* 206 (M^+). Found: C, 75.37; H, 8.89%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%.

*(E)- and (Z)-7-Propylidene-5-oxadispiro[2.0.4.4]dodecan-6-one (**4d**) and (**4e**).* The reaction of **3** (6.0 g, 33.3 mmol) and propionaldehyde (2.3 g, 33.3 mmol) gave the crude α-(1-hydroxypropyl)-γ-lactone (6.4 g, 80%: IR 3450, 1740 cm^{-1}). Dehydration of the alcohol by method A (the mesylate: IR 1740, 1350, 1160 cm^{-1}) gave the mixture of *E*-isomer **4d** and *Z*-isomer **4e** which were separated by column chromatography (SiO_2, 3% ether–petroleum ether). **4d** (30% from **3**): IR 3050, 1740, 1670 cm^{-1}; NMR δ 0.10—1.00 (m, 4H), 1.10 (t, 3H), 1.28—2.00 (m, 8H), 2.18 (m, 2H), 2.56 (m, 2H), 6.48 (m, 1H); MS *m/e* 220 (M^+). Found: C, 76.03; H, 9.21%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%. **4e** (20% from **3**): IR 3050, 1735, 1660 cm^{-1}; NMR δ 0.10—1.00 (m, 4H), 1.03 (t, 3H), 1.16—2.00 (m, 8H), 2.64 (m, 4H), 6.00 (m, 1H); MS *m/e* 220 (M^+). Found: C, 76.14; H, 9.24%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

*7-Isopropylidene-5-oxadispiro[2.0.4.4]dodecan-6-one (**4f**).* The reaction of **3** (5.0 g, 27.8 mmol) and acetone (1.6 g, 27.8 mmol) gave the crude α-(1-hydroxy-1-methylethyl)-γ-lactone (6.4 g, 97%: IR 3450, 1735 cm^{-1}). Dehydration of the alcohol by method B gave the crude α-isopropylidene-γ-lactone **4f** which was purified by column chromatography (SiO_2, 5% ether–petroleum ether) to afford 3.2 g of **4f** (52% from **3**): mp 70—71 °C (recrystallized from petroleum ether); IR (KBr) 3050, 1730, 1650 cm^{-1}; NMR δ 0.10—1.00 (m, 4H), 1.15—1.80 (m, 8H), 1.84 (m, 3H), 2.20 (m, 3H), 2.58 (m, 2H); MS *m/e* 220 (M^+). Found: C, 76.11; H, 9.28%. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15%.

*Tetrahydropyran-2-yl Acetonyl Ether (**5**).* A solution of hydroxyacetone (10 g, 0.135 mol) in 200 ml of dry CH_2Cl_2 containing 1.0 g of *p*-toluenesulfonic acid was treated at 0 °C with 3,4-dihydro-2*H*-pyran (13.6 g, 0.162 mol). After stirring at 0 °C for 3.5 h, the reaction was quenched by the addition of saturated $NaHCO_3$ solution and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and concentrated *in vacuo* leaving the crude THP-ether **5**. Column chromatography (SiO_2, 20% ether–petroleum ether) followed by distillation gave 12.0 g of pure **5** in 57% yield: bp 64—66 °C/267 Pa; IR 1710, 1110, 1060, 1010 cm^{-1}; NMR δ 1.36—2.00 (m, 6H), 2.10 (s, 3H), 3.52 (m, 1H), 3.80 (m, 1H), 4.00 (m, 2H), 4.58 (t, 1H); MS *m/e* 156 (M^+-2). Found: C, 60.56; H, 8.99%. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%.

*(E)- and (Z)-7-(2-hydroxyisopropylidene)-5-oxadispiro[2.0.4.4]dodecan-6-one (**4g**) and (**4h**).* The reaction of **3** (6.0 g 33.3 mmol) and **5** (5.3 g, 33.3 mmol) gave the crude alcohol (11.2 g, quantitatively: IR 3450, 1750, 1010 cm^{-1}). Dehydration of the alcohol by method B afforded the crude THP-ether (**6**) (10.1 g, 95% from **3**: IR 3050, 1720, 1650, 1010 cm^{-1}). The above ether **6** was dissolved in 100 ml of 60% aqueous acetic acid and the solution was stirred at 45 °C for 3 h. The reaction mixture was neutralized with saturated $NaHCO_3$ solution and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and concentrated *in vacuo* leaving the mixture of *E*-isomer **4g** and *Z*-isomer **4h**. Separation by column chromatography (SiO_2, 20% ether–petroleum ether) gave 0.7 g of **4g** and 2.4 g of **4h** (9% and 31% from **3**, respectively). **4g**: IR 3400, 3050, 1730, 1650 cm^{-1}; NMR δ 0.10—0.90 (m, 4H), 1.08—2.04 (m, 8H), 2.16 (m, 3H), 2.64 (m, 2H), 2.74 (broad s, 1H), 4.10 (s, 2H); MS *m/e* 236 (M^+). Found: C, 70.94; H, 8.58%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%. **4h**: IR 3400, 3050, 1720, 1650 cm^{-1}; NMR δ 0.10—0.95 (m, 4H), 1.08—1.85 (m, 8H), 1.90 (m, 3H), 2.62 (m, 2H), 3.48 (broad s, 1H), 4.36 (s, 2H); MS *m/e* 236 (M^+). Found: C, 70.95; H, 8.57%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

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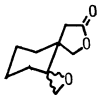
4) Also, we already reported the synthesis of 1,6-dioxadispiro[2.0.4.4]dodecan-7-one (**7**), having a spiro epoxy ring, which is a useful intermediate for the synthesis of α-alkylidene-γ-butyrolactones.[5)]



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