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HIGHLY REGIO- AND STEREOSELECTIVE RING-OPENING REACTION OF γ-ALKENYL-γ-BUTYROLACTONES USING ALLYLSILANES-TRIMETHYLOXONIUM SALT TO AFFORD METHYL (E)-4,8-ALKADIENOATES

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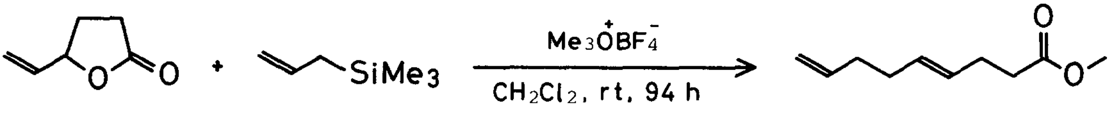
Summary: *γ-Alkenyl-γ-butyrolactones reacted regio- and stereoselectively with allyltrimethylsilanes in the presence of trimethyloxonium tetrafluoroborate to afford methyl (E)-4,8-alkadienoates in high yields. Synthetic utility of the present reaction was demonstrated by the synthesis of β-sinensal.*

Recently, organic syntheses utilizing allylsilanes have been considerably developed. Allylation of acetal, halide, or aldehyde with allylsilanes in the presence of Lewis acid such as $TiCl_4$, $SnCl_4$, or $AlCl_3$ are well known,[1] which consists of the electrophilic substitution with allylic rearrangement. On the other hand, to our knowledge only one example has been reported for the electrophilic reaction of allylsilane with allylic derivative, which accompanied with allylic rearrangement of the substrate.[2] Here we wish to report the highly regio- and stereoselective ring-opening reaction of γ-alkenyl-γ-butyrolactones with allylsilanes in the presence of trimethyloxonium tetrafluoroborate to give methyl (*E*)-4,8-alkadienoates in high yields.

Although the ring-opening reaction of γ-alkenyl-γ-butyrolactones with diallylcuprate was already developed in our laboratory,[3] the desired product, 4,8-nonadienoic acid was not obtained with high stereoselectivity and in a satisfactory yield, because of the lack of thermal stability of diallylcuprate. On the contrary, allylsilanes are thermally stable compound, but the nucleophilic reactivity is poor. Therefor, in the ring-opening reaction of γ-alkenyl-γ-butyrolactones, it is necessary to activate the lactones. We found that the use of trimethyloxonium tetrafluoroborate,[4] known as the methylating agent of γ-butyrolactone,[5] as the activator gave dramatic good results, although no formation of the desired alkadienoic acid was observed by the use



of Lewis acid such as $TiCl_4$, $SnCl_4$, $AlCl_3$, $Me_3SiOSO_2CF_3$, or Me_3SiI as the activator.

The representative example is as follows: To a suspension of trimethyloxonium tetrafluoroborate (2 mmol) in CH_2Cl_2 (9 ml) was added a solution of γ-vinyl-γ-butyrolactone (1 mmol) and allyltrimethylsilane (3 mmol) in CH_2Cl_2 (6 ml) at room temperature. The mixture was stirred at the same temperature for 94 h and then quenched by adding saturated aqueous $NaHCO_3$. After the usual work-up, methyl 4,8-nonadienoate was obtained quantitatively. The carbon-carbon double bond newly formed in C-4 position of the product was assigned as exclusive E configuration by the absorption at 950 cm^{-1} in IR spectrum and by comparison in glpc with the authentic sample.[6] The regioisomer, methyl 4-vinyl-6-heptenoate formed by the attack of allylsilane to γ-position of the lactone, was not detected. Accordingly, this ring-opening reaction was found to possess high regio- and stereoselectivities.

The use of other solvents such as benzene, ether, and nitromethane did not give good results. The use of triethyloxonium tetrafluoroborate in place of trimethyloxonium tetrafluoroborate resulted in a low yield (61%). When the reaction mixture was refluxed in CH_2Cl_2 with stirring, the yield of methyl (*E*)-4,8-nonadienoate was decreased to 83%, but the reaction time could be shortened for 8 h.

Results obtained from the reaction of various substituted allyltrimethylsilanes[7] and γ-alkenyl-γ-butyrolactones[8] were shown in the Table, which were carried out at room temperature in CH_2Cl_2. As shown in the Table, the desired

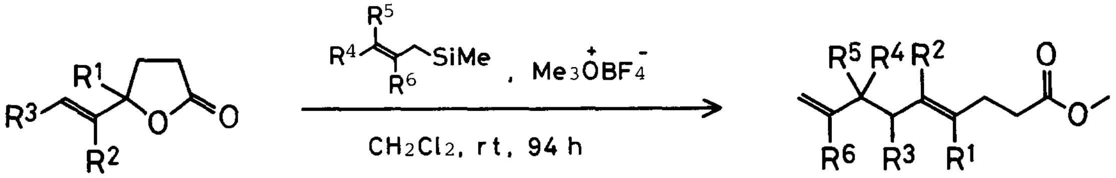


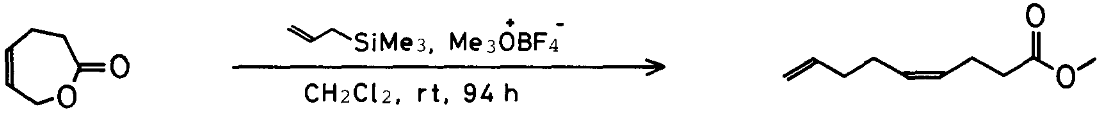
Table. Yields of Methyl (*E*)-4,8-Alkadienoates by the Reaction of γ-Alkenyl-γ-butyrolactones with Allylsilanes-Trimethyloxonium Salt[a]

Run	R^1	R^2	R^3	R^4	R^5	R^6	Yield(%)[b]
1	H	H	H	H	H	H	100
2	H	H	CH_3	H	H	H	85
3	H	CH_3	H	H	H	H	81
4	H	H	H	H	H	CH_3	90
5	H	H	H	CH_3	CH_3	H	93
6	H	H	H	H	H	CH_2=CH	74
7	CH_3	H	H	H	H	H	74

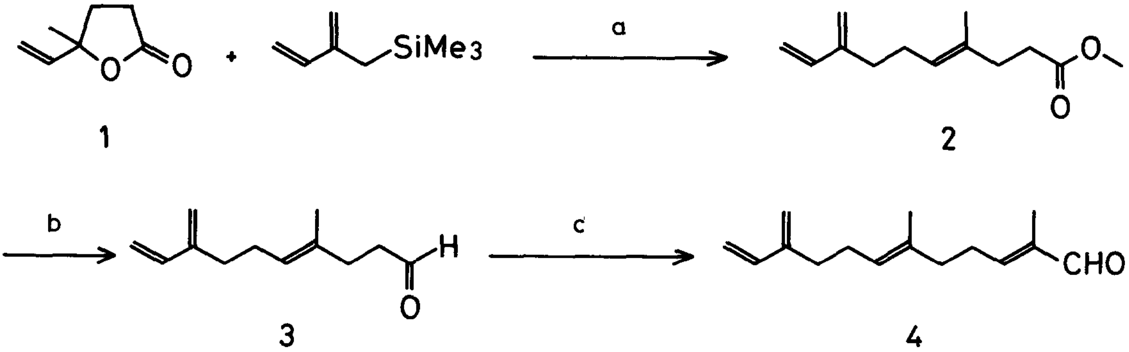
[a] All reactions were performed on 1 mmol scale with the same procedure as described in the text. The products were identified by NMR and IR spectra, and were confirmed as an exclusive E isomer by glpc analysis. [b] Isolated yields by silica-gel TLC.

methyl (*E*)-4,8-alkadienoates were obtained in high yields with complete regio- and stereoselectivities, even when either lactones or allylsilanes with methyl substituent were used.

On the other hand, when (*Z*)-4-hexenolide[9] instead of γ-alkenyl-γ-butyrolactone was used in the reaction with allyltrimethylsilane and trimethyloxonium tetrafluoroborate, ring-opening reaction of the lactone without allylic rearrangement occured to give methyl 4,8-nonadienoate with exclusive Z configuration in a yield of 87%.



To demonstrate the utility of the present reaction, the synthesis of the sesquiterpene aldehyde β-sinensal,[10] an important contributor to the aroma and taste of Chinese orange oil, was achieved in a short step using the highly regio- and stereoselective ring-opening reaction of γ-methyl-γ-vinyl-γ-butyrolactone (**1**). The reaction of **1**[11] (131 mg, 1.04 mmol) with 2-trimethylsilylmethyl-1,3-butadiene[12] (438 mg, 3.12 mmol) in the presence of trimethyloxonium tetrafluoroborate (154 mg, 1.04 mmol) in CH_2Cl_2 (10 ml) at room temperature with stirring for 71 h followed by the usual work-up gave methyl (*E*)-4-methyl-8-methylene-4,9-decadienoate (**2**) (140 mg, 0.676 mmol) in 65% yield. The ester was reduced with diisobutylaluminum hydride (0.676 mmol) in THF toluene to produce the corresponding aldehyde (**3**) (100 mg, 0.561 mmol) in 83% yield. The Wittig reaction of **3** with α-formylethylidenetriphenylphosphorane[13] in refluxing benzene afforded the desired *trans,trans*-β-sinensal (**4**) (100 mg, 0.460 mmol) in a yield of 82%. All the spectral data were consistent with those recorded.[14]



a Me_3OBF_4, CH_2Cl_2, rt/71 h; b *i*-Bu_2AlH, THF-toluene, -78 °C/2.7 h; c Ph_3PCCH_3CHO, C_6H_6, reflux/22 h

Thus the reaction of γ-alkenyl-γ-butyrolactones with allylsilanes in the presence of trimethyloxonium tetrafluoroborate proceeds highly regio- and stereoselectively in a mild condition to afford methyl (*E*)-4,8-alkadienoates in high yields. As shown in the short step synthesis of β-sinensal, this reaction offers a highly selective synthetic method of natural products.

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6. Authentic sample of E configuration rich mixture was prepared by esterification of 4,8-nonadienoic acid synthesized according to our method,[3] and was used in comparison with the product by capillary glpc analysis (FFAP, 50 m).
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9. (*Z*)-4-Hexenolide was prepared according to the following paper; S. F. Birch, R. A. Dean, and N. J. Hunter, *J. Org. Chem.*, 23, 1390 (1958). Although only γ-vinyl-γ-butyrolactone has been reported to obtain by distillation of 2-vinylcyclopropane-1,1-dicarboxylic acid in the paper, it was found that the products by the same manner were the mixture of (*Z*)-4-hexenolide and γ-vinyl-γ-butyrolactone. They were separated by silica-gel column chromatography, in which the ratio of *n*-hexane-ether as an eluent was gradually changed from 5:1 to 1:3. New compound, (*Z*)-4-hexenolide was characterized by analytical and spectroscopic methods; NMR (CCl_4) δ 2.5 (2H, m, CH_2CO), 2.8 (2H, m, $CH_2\overset{|}{\underset{|}{C}}CO$), 4.6 (2H, m, CH_2OCO), 5.8 (2H, m, CH=CH); IR (neat) 1730 cm^{-1} (C=O), Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.45; H, 6.92.
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