in the ground state. For better understanding of this selectivity, kinetic studies on these molecules are currently in progress.

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3. These compounds were synthesized by standard procedures; Compounds 1 and 2 were prepared by the condensation of acetone with the corresponding arylacetonitriles, and consecutive 1,4- and 1,2- addition of phenyl Grignard reagents, followed by hydrolysis. Overall isolated yields were 12 and 18%, respectively. Compound 3 was prepared by α-benzylation of *o*-tolylacetonitrile and 1,2- addition of phenyl Grignard reagent, followed by hydrolysis. Overall yield was 42%. Spectroscopic data of compound 1; ¹H NMR (200 MHz, CDCl₃) δ 7.67 (2H, d), 7.1-7.5 (12H, m), 5.18 (1H, s), 2.09 (3H, s), 1.70 (3H, s), 1.50 (3H, s), IR (CCl₄), 1694 (C=O) cm⁻¹, Mass 77, 91, 105, 119, 210. Molecular ion peak was not detected. Spectroscopic data of compound 2; ¹H NMR (200 MHz, CDCl₃) δ 7.72 (2H, d), 7.1-7.45 (13H, m), 5.00 (1H, s), 1.60 (3H, s), 1.43 (3H, s), IR (CCl₄), 1692 (C=O) cm⁻¹, Mass 77, 91, 105, 119, 196. Molecular ion peak was not detected. Spectroscopic data of compound 3; ¹H NMR (200 MHz, CDCl₃) δ 7.77 (2H, d), 7.05-7.47 (12H, m), 4.93 (1H, dd, *J*=6.5, 7.6 Hz), 3.55 (1H, dd, *J*=7.6, 13.6 Hz), 2.95 (1H, dd, *J*=6.5, 13.6 Hz), 2.25 (3H, s), IR (CCl₄), 1688 (C=O) cm⁻¹, Mass 77, 91, 105, 195, 300 (M⁺).
4. ¹H NMR spectra of authentic samples were obtained separately and were compared with those of photoproducts. These were also same as the published data. Ref. 6 and Pouchert, C. J.; Behnke, J. In *The Aldrich Library of ¹³C and ¹H FT NMR Spectra*; Aldrich chemical Co. Inc.; Inc.; U.S.A.; 1993, Chemical yields of 5 and 6 in the photolysis of compound 1 were 40 and 45%, respectively. Chemical yields of 5, 8 and 9 in the photolysis of compound 2 were 30, 10 and 12%, respectively.
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Radical Mediated Alkylations of Vinyl Epoxides

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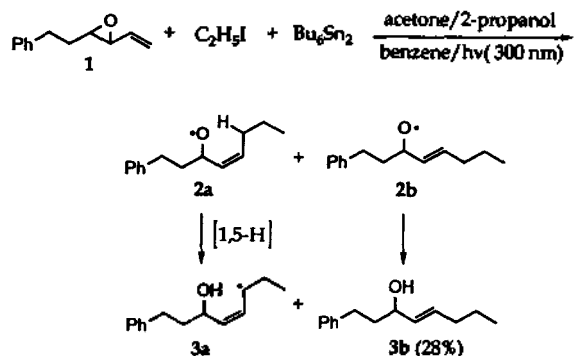Taejon 305-701, Korea*

The reaction of vinyl epoxides with various organometallic reagents such as organolithium,[1] organocopper,[2] and organopalladium reagents[3,4] is very useful in organic synthesis. However, radical reactions of vinyl epoxides have received little attention.[4] Recently, we have studied the radical reactions of vinyl epoxides utilizing 1,5-Bu₃Sn group or 1,5-hydrogen atom transfer.[5]
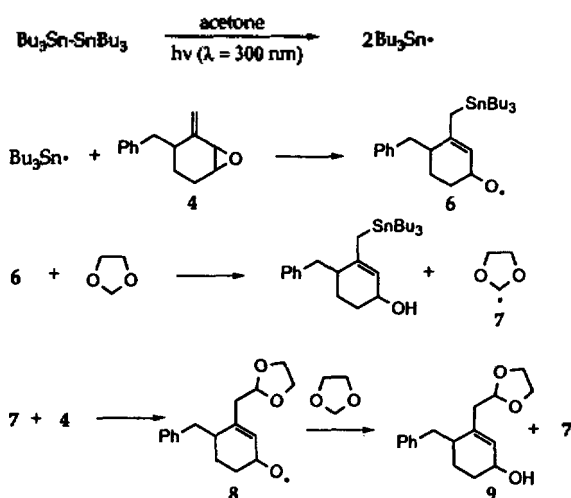
Concerning radical mediated alkylations of vinyl epoxdes, it was reported that a cycloalkyl radical had attacked a vinyl epoxide to yield the allylic alcohol in only 13% yield.[4a] The similar alkylation was also achieved with trialkylborane in the presence of oxygen.[6] However, the yield was relatively low and the generality of the reaction was not demonstrated. Recently, radical alkylation of vinyl epoxides was successfully carried out with stable carbon-centered radicals using amineborane complex.[7]

In connection with our interest in radical reactions of vinyl epoxides,[5,8] we studied the possibility of intermolecular radical alkylations of vinyl epoxides with alkyl radicals. However, initial results were discouraging. When the radical reactions of vinyl epoxides were carried out with alkyl iodides and Bu₃SnH/AIBN under highly diluted conditions using a syringe pump technigue, alkyl radicals reacted with Bu₃SnH before attacking vinyl epoxides, yielding the direct reduction products along with the starting vinyl epoxides. Therefore, a clean generation of tributyltin radical in the absence of any efficient radical scavengers like Bu₃SnH was required. A recent report on selective homolytic cleavage of bis-tributyltin using a photosensitizer such as acetone or *p*-methoxyacetophenone under mild irradiation[9] was suited for our purpose. Intermolecular radical alkylations involving the addition of alkyl radicals to the double bonds have been sucessfully performed using this procedure.[10]

When the radical reaction of acyclic vinyl epoxide 1 was carried out with ethyl iodide in benzene using bis-tributyltin/acetone/2-propanol system under irradiation (300 nm), 3b was isolated in only 28% yield. The low yield with 1 may result from facile 1,5-hydrogen transfer in 2a from carbon to oxygen as shown in Scheme 1. The resulting allylic radical 3a would be reluctant to abstract hydrogen atom from 2-propanol due to its low reactivity. Much better results were obtained with endo vinyl epoxide 4. When the radical reaction of 4 was carried out with ethyl iodide under the same conditions, the alkylated product 5a was obtained in 63% yield along with 5b (4%) and 5c (9%) as side products. We envisioned that 5b might be formed by ejection of hydrogen atom from an intermediate alkoxy radical and 5c might result from attack of tributyltin radical to 4, although an exact mechanism awaits further studies. As shown in Table 1, several alkyl iodides were employed and similar results were

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Scheme 1.

Scheme 2.

Table 1. Alkylation of *endo* Vinyl Epoxide with Alkyl Iodides

RI	yields, %		
	5a	5b	5c
CH₃I	52	5	7
CH₃CH₂I	63	4	9
Ph(CH₂)₂I	48	8	14
(CH₃)₂CH-I	60	0	3
⬡—I	65	6	5

Table 2. Alkylation of *endo* Vinyl Epoxide with Acetals or Ethers[a]

AH	time, h	yield (%)	AH	time, h	yield (%)
(furan-O-H)	2	77	(pyran-O-H)	3	57
(dioxolane-H)	1	85	(dioxane-H)	3	61
H₃CO-O-OCH₃ H	2.5	67	H₃CO-OCH₃ H	29	15
H-C(OCH₃)₃	24	17			

[a] AH was used as solvent.

obtained.

Our next attention was given to the radical alkylation of vinyl epoxides with acyclic and cyclic acetals.[11] Our approach is outlined in Scheme 2 and the reaction was initiated by tin radical addition to the vinyl epoxide, followed by epoxide ring opening to generate alkoxy radical 6. The alkoxy radical would abstract hydrogen atom from 1,3-dioxolane to produce 7 which would add to a vinyl epoxide to generate alkoxy radical 8. Finally, it would react with 1,3-dioxolane to afford 9 together with 1,3-dioxolanyl radical to become a chain process. Such a chain process would require only a catalytic amount of bis-tributyltin to initiate this reaction and the formation of undesired side products would be minimized.

The radical alkylations of vinyl epoxides with cyclic and acyclic ethers or acetals were carried out with bis-tributyltin/acetone under irradiation. It is noteworthy that ethers and acetals tested in this study were used as a solvent as well as a reagent. The effectiveness of cyclic and acyclic acetals was determined with endo vinyl epoxide 4 and the experimental results are summarized in Table 2. The best result was obtained with 1,3-dioxolane and relatively low yields were obtained with acyclic acetals. The present results are agreeable with the recent report on relative rates of intermolecular hydrogen atom abstraction by *t*-butoxy radical with several types of acetals and ethers.[12]

Since initial studies using 1,3-dioxolane were promising, we performed radical mediated alkylation with several endo vinyl epoxides to demonstrate the effectiveness of the present method. The experimental results are summarized in Table 3 and several features are noteworthy. First, the reaction can be also carried out with 1,3-dioxolane (5 equiv) in refluxing benzene as a solvent. When 1,3-dioxolane was used as a solvent, the yield was slightly better, ranging from 54% to 85%. Second, the reaction worked well with several epoxy vinyl acetates and an epoxy vinyl phosphate. This process is synthetically equivalent to formylation of α,β-unsaturated cyclic ketones at α' position. Third, 4-methoxy-acetophenone (0.2 equiv) can be also effectively utilized as a photosensitizer. Finally, in the case of an exo vinyl epoxide, the reaction did not take place due to facile transfer of 1,5-Bu₃Sn group from carbon to oxygen.[5a] A typical procedure is as follows. To a degassed solution of 1,3-dioxolane (2 mL) were added a vinyl epoxide (1.0 equiv), Bu₃SnSnBu₃ (0.1 equiv), and acetone (3 equiv). The solution was irradiated for 2 h in a Rayonet reactor (300 nm).

In conclusion, we have shown that the intermolecular radi-

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Table 3. Alkylation of *endo* Vinyl Epoxides with 1,3-Dioxolane

vinyl epoxides	products	yields,[a] %	vinyl epoxides	products	yields,[a] %
		75 (71)			74 (68)
		54			71 (64)
		85 (76)			75
		73 (66)			41
		63 (60)			46 (43)

[a]The numbers in the parentheses indicate the isolated yield using 5 equiv of 1,3-dioxolane in refluxing benzene.

cal reactions of endo vinyl epoxides with alkyl iodides and 1,3-dioxolane proceed by mild photochemical generation of tributuyltin radical and are very useful for introducing alkyl groups and a formyl group to a variety of structurally different vinyl epoxides.

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Conversion of Carboxylic Esters to Aldehydes by Sodium Gallium Hydride

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The synthesis of aldehydes from carboxylic esters is one of the important reaction in organic synthesis. Many reducing agents have been tested, however, only a few reagents have achieved for the transformation of carboxylic esters to the corresponding aldehydes. The representative metal hydrides for such purpose are diisobutylaluminum hydride (DIBAH),[1] sodium diisobutylaluminohydride,[2] lithium tri-*tert*-butoxy-aluminum hydride (LTBA),[3] and bis(dialkylamino)aluminum hydrides.[4] Of these reagents, LTBA reduces aliphatic phenyl esters to corresponding aldehydes in yields of approximately 70%, but it can not reduce aromatic esters. Although diaminoaluminum hydride is effective for both aliphatic and aromatic esters and gives 50-80% yields of aldehydes, the reaction requires the longer reaction time (6-12 h), usually at elevated temperature (65 °C). And DIBAH reduces aliphatic and aromatic esters to corresponding aldehydes in yields of aldehydes (48-88%) at very low temperature (−70 °C). Recently, sodium diethylpiperidinohydroaluminate[5] and lithium tris(diethylamino)aluminum hydride[6] are reported to be good reagents for the partial reduction of carboxylic esters to the corresponding aldehydes.

In 1977, Dilts and Nutt[7] first reported the synthesis of sodium gallium hydride. The sodium gallium hydride is prepared from lithium gallium hydride.

$$LiGaH_4 + NaH \xrightarrow{\text{THF}} NaGaH_4 + LiH \downarrow$$

In the course of exploring the reducing properties of sodium gallium hydride, we observed that ethyl caproate and ethyl benzoate consumed one hydride rapidly for reduction, but the further reaction proceeded slowly. This results suggested the possibility of aldehyde synthesis from carboxylic ester using this reagent.

As shown in Table 1. the reagent reduced aliphatic carboxylic esters to the corresponding aldehydes in yields of 75-87%. The reduction of aromatic esters by this reagent pro-

6169.