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TRANSFORMATION OF B-ALKENYL-B-PROPIOLACTONES INTO CYCLOPROPYLACETIC ACIDS UTILIZING HYDROBORATION

Masatoshi KAWASHIMA and Tamotsu FUJISAWA* Chemistry Department of Resources, Mie University, Tsu, Mie 514

The reaction of β -alkenyl- β -propiolactones with 9-borabicyclo [3.3.1]nonane and subsequent treatment with sodium methoxide gave cyclopropylacetic acids in good yields.

 β -Vinyl and β -isopropenyl- β -propiolactones are useful synthetic blocks for the synthesis of (E)-3-alkenoic acids. For example, β -vinyl- β -propiolactone reacts with Grignard reagents in the presence of a copper(I) catalyst to give (E)-3-alkenoic acids¹⁾ and the synthetic utilities of this reaction are demonstrated by the synthesis of queen substance and Royal jelly acids.²⁾ Reaction of β -isopropenyl- β -propiolactone with organocuprates is also applied to the synthesis of homogeranic and homofarnesylic acids which are the precursors of various terpenoids.³⁾ Here we wish to report the new synthetic method of cyclopropylacetic acids accessible for natural product synthesis using the carbon skeleton transformation of β -alkenyl- β -propiolactones. Although cyclopropylacetic acids are expected to be obtained by the Simmons-Smith reaction of 3-alkenoic acids, practically cyclopropylacetic acid is obtained only in a low yield from 3-butenoic acid even by the use of large excess of the reagent for the olefin.⁴⁾

To a solution of β -vinyl- β -propiolactone in THF was added a solution of 9borabicyclo[3.3.1]nonane (9-BBN) in THF at room temperature and the mixture was stirred for 6 h. Then, without isolation of the intermediate trialkylborane, treatment of the mixture with sodium methoxide at the same temperature for 12 h afforded cyclopropylacetic acid in a yield of 76% after usual work-up.⁵⁾



The other hydroborating agents such as dicyclohexylborane, 3,6-dimethylborinane, and bis-(3-methyl-2-butyl)borane, and the other bases such as lithium methoxide, sodium acetate, and methyllithium were used in the present method. As the result, the combination of 9-BBN and sodium methoxide gave the best yield. With respect to the stereochemistry, the use of 3,6-dimethylborinane showed the best effect for obtaining the *cis* isomer in the reaction of β -isopropenyl- β -propiolactone, while the *trans* isomer was preferably obtained by the use of dicyclohexylborane, although the yields were not so good. In order to expand the synthetic utility of the present reaction, various β -alkenyl- β -propiolactones, which were



Table 1.

 Transformation of β-Alkenyl-β-propiolactones into Cyclopropylacetic Acids^{a)}

R	Dialkylborane	Product ^{b)}	Yield/%	cis	: trans c)
		0			
Н	9 - BBN		76		
CH 3	9-BBN		54	67	: 33
CH 3	ВН	С	39	71	: 29
CH 3	(∕→)-2 BH	Дон он	27	28	: 72
C ₂ H ₅	9-bbn		77	53	: 47
<i>n−</i> C₄H ₉	9-BBN		50	51	: 49
$n - C_6 H_{13}$	9-BBN		49	53	: 47

a) All reactions were performed on 2 mmol scale. The molar ratio of the lactone, dialkylborane, and the base is 1.0:1.5:1.8. b) Products were isolated by silica-gel TLC and identified by IR and NMR spectra. c) Product ratio was determined by capillary glpc analysis (F.F.A.P. 50 m).

easily prepared from 2-methylenealkanal and ketene,⁶⁾ were used to this transformation into cyclopropylacetic acids as shown in Table. Even when a long chain group such as hexyl group was substituted at the β -vinyl group of β -vinyl- β -propiolactone, the corresponding cyclopropylacetic acid was obtained. In this case, the obtained acid is known as cascarillic acid⁷⁾ isolated from essential oil of *Croton eluteria* Benett.

As mentioned above, this transformation of β -alkenyl- β -propiolactones can be performed by a simple procedure under mild conditions using very available starting materials to afford the useful synthetic method of cyclopropylacetic acids.

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