CHEMISTRY LETTERS, pp. 1273-1274, 1983.

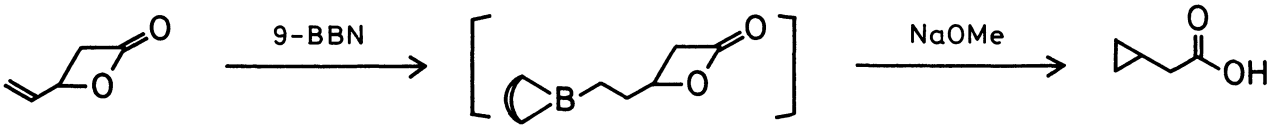
TRANSFORMATION OF β-ALKENYL-β-PROPIOLACTONES INTO CYCLOPROPYLACETIC ACIDS UTILIZING HYDROBORATION

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 acids[1] 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 9-borabicyclo[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

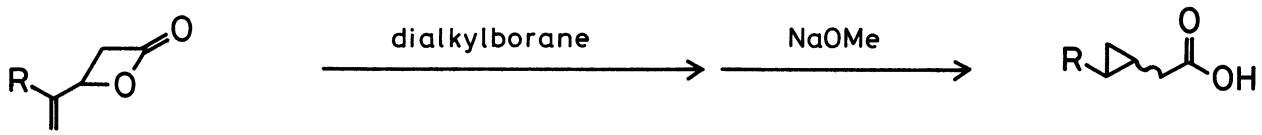
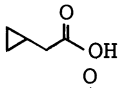
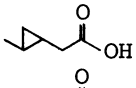
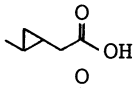
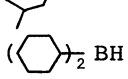
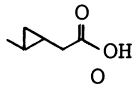
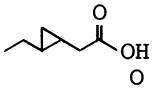
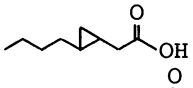
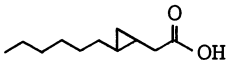


Table 1. Transformation of β-Alkenyl-β-propiolactones into Cyclopropylacetic Acids[a)]

R	Dialkylborane	Product[b)]	Yield/%	*cis* : *trans* [c)]
H	9-BBN		76	
CH_3	9-BBN		54	67 : 33
CH_3			39	71 : 29
CH_3			27	28 : 72
C_2H_5	9-BBN		77	53 : 47
n-C_4H_9	9-BBN		50	51 : 49
n-C_6H_{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 acid[7)] 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.

References

1) T. Sato, M. Takeuchi, T. Itoh, M. Kawashima, and T. Fujisawa, *Tetrahedron Lett.*, 22, 1817 (1981).
2) T. Fujisawa, T. Sato, and T. Itoh, *Chem. Lett.*, 1982, 219.
3) T. Fujisawa, T. Sato, M. Kawashima, and M. Nakagawa, *Chem. Lett.*, 1981, 1307.
4) I. M. Takakis and Y. E. Rhodes, *J. Org. Chem.*, 43, 3496 (1978).
5) Similar transformation of allyl chloride into cyclopropane has been reported; H. C. Brown, "Organic Syntheses *via* Boranes," Wiley, New York (1975), p. 125.
6) β-Alkenyl-β-propiolactone was prepared according to the following papers: J. H. McCain and E. Marcus, *J. Org. Chem.*, 35, 2414 (1970); A. F. Noels, J. J. Herman, and P. Teyssié, *ibid.*, 41, 2527 (1976).
7) S. R. Wilson and K. A. Prodan, *Tetrahedron Lett.*, 1976, 4231.

(Received June 20, 1983)