Tetrahedron Letters,Vol.30,No.38,pp 5153-5156,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

ORGANIC SYNTHESIS USING HALOBORATION REACTION XV. A NEW SYNTHESIS OF α,β-UNSATURATED ESTERS BY THE HIGHLY CHEMOSELECTIVE REACTION OF B-I-9-BBN-ETHOXYETHYNE ADDUCT WITH ALDEHYDES

Yoshitaka Satoh, Takao Tayano, Shoji Hara, and Akira Suzuki*
Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo 060, Japan

Abstract: A haloboration adduct, formed by the reaction of B-iodo-9-borabicyclo[3.3.1]nonanes with ethoxyethyne reacts with aldehydes chemoselectively under very mild conditions. The subsequent hydrolytic work-up affords trans-α,β-unsaturated esters in good yields.

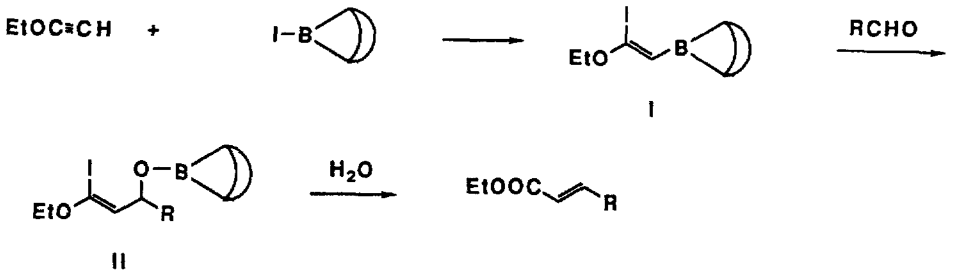
The transformation of aldehydes to two carbon-homologated α,β-unsaturated esters is one of the most important reactions (eq.1), and the modified Wittig reaction involving phosponate carbanion is most frequently used.[1] However, such reaction requires basic conditions and base sensitive substrates can not be applied. Described herein is a new reaction of B-iodo-9-borabicyclo[3.3.1]nonanes (B-I-9-BBN's)[2] and ethoxyethyne adducts with aldehydes which gives trans- α,β-unsaturated esters with high chemoselectivity.

$$\mathrm{RCHO} \longrightarrow \mathrm{RCH{=}CHCOOEt} \qquad (1)$$

Addition of one equivalent of ethoxyethyne to a pentane solution of B-I-9-BBN at -78 °C gave white precipitate which reacted with benzaldehyde to give trans-ethyl cinnamate in 89 % yield. A series of aldehydes were subjected to this reaction , and the results are summarized in the Table.

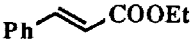
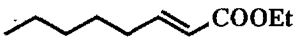
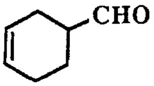
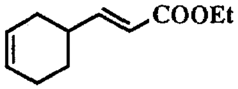
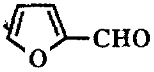
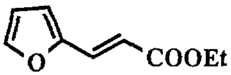
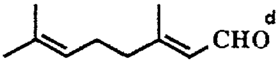
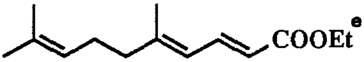
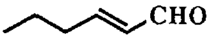
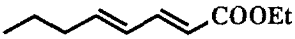
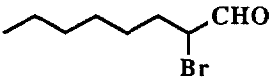
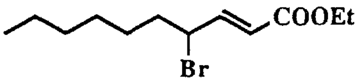
The remarkable feature of this reaction is the high chemoselectivity, and no reactions were observed with 2-octanone, acetophenone, benzoyl chloride, ethyl benzoate, valeronitrile and benzalaniline.[4] Moreover under this mild reaction conditions, even bromoaldehydes which are highly base sensitive, gave the desired unsaturated esters without any change on bromo functionality (Entries 7 and 8 in Table).

The thermally unstable nature of the haloboration adduct prevents its full characterization[6], but we have postulated the plausible reaction pathway in eq. 2.



(2)

Table The Synthesis of trans- α,β -Unsaturated Esters

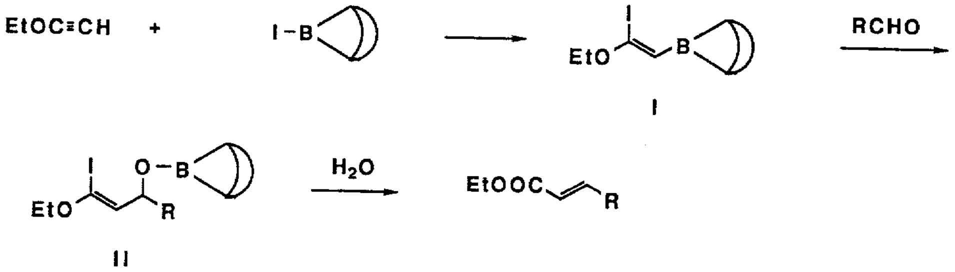
Entry	Aldehyde	Product[a]	Yield,%[b]	I.P.,%[c]
1	PhCHO		(89)	99
2			77	99
3			80	99
4			76	99
5	[d]	[e]	85	—
6			82	96
7			66	99
8			70	—[f]

a) All the products gave satisfacory IR, ^{1}HNMR, and high resolution mass spectra.

b) Isolated yields after purification by tlc. In a parenthesis is shown a glpc yield.

c) Isomeric purity determined by capillary glpc analyses. d) A mixture of (E)- and (Z)-isomers were used. (e) A mixture of (2E,4E)- and (2E,4Z)-isomers.

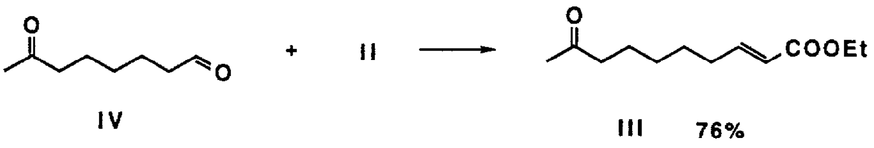
(f) The product decomposes on glpc analysis.



(2)

The following procedure for the synthesis of ethyl (E)-cinnamate is representative: To a solution of B-I-9-BBN (0.24 g, 1.0 mmol) in 5 ml of pentane was added ethoxyethyne (70 mg, 1.0 mmol) at -78 °C with stirring. The resulting white solid was stirred for 30 min at -78 °C. Then benzaldehyde (106 mg, 1.0 mmol) was added, and the reaction mixture was stirred at -78 °C for 15 min and then at room temperature for 30 min. The mixture was cooled to 0 °C and treated with EtOH (1 ml) and water (3 ml). Analysis of the organic layer by glpc revealed that ethyl (E)-cinnamate had been formed in 89% yield with 99% of stereoselectivity.

We applied this method for the synthesis of ethyl (E)-9-oxodecenoate (III), one of the "queen substances"[11], to demonstrate the highly chemoselective nature, as shown in eq. 3. The expected pheromone was obtained in 76 % yield from the ketoaldehyde (IV) directly without any protection-deprotection of the keto functionality. No product originated from the attack of the adduct to the keto moiety was found in the reaction mixture .

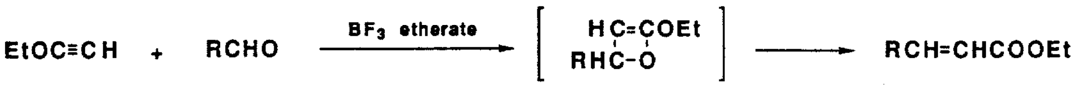


(3)

Further studies on the present novel reaction is in progress.

References and Notes

1. W. S. Wadsworth, Jr. Organic Syntheses, 25, 73 (1977).
2. B-I-9-BBN was prepared by the reaction of 9-BBN with dry hydrogen iodide according to the literature[3] and distilled twice under nitrogen atmosphere.
3. H. C. Brown and S. V. Kulkarni, J. Organomet. Chem., 168, 281 (1979)
4. J. F. Arens and others reported[5] that ethoxyethyne reacts with carbonyl compounds in the presence of BF_3 etherate catalyst to give α,β-unsaturated esters, and the oxete (V) was proposed to be the possible reaction intermediate. However, in their reactions, the characteristic high chemoselectivity was not observed,



V

(5) (a) J. F. Arens, Advances in Organic Chemistry; 2, 117 (1960). (b) G. Vollema, J. F. Arens, Rec. Trav. Chim., 82, 305 (1963). (c) H. Vieregge, H. M. Schmidt, J. Renema, H. J. T. Bos, J. F. Arens, Rec.Trav.Chim. 85, 921 (1966). (d) Y. I. Baukov, G. S. Zaitseva, L. I. Livantsova, R. A. Bekker, K. A. Savost'yanova, G. I. Oleneva, I. F. Lutsenko, Zh. Obshch. Khim. 51, 1304 (1981). (e) J. Pornet, B. Khouz, L. Miginiac, Tetrahedron Lett., 26, 1861 (1985).

(6) Ethoxyethyne and B-I-9-BBN adduct (I) was unstable and decomposed at room temperature immediately. But the alkynylated derivative (VI) could be isolatedstably by the following reactions and characterized fully.

I

VI

(7) Haloboration reactions of alkynes with B-halo-9-BBN see: S. Hara, H. Dojo, S. Takinami, and A. Suzuki, Tetrahedron Lett., 24, 731 (1983).

(8) The 1,2- addition of organoboranes to aldehydes other than allylic ones is usually does not occur, but as for the B-alkenyl-9-BBN, 1,2-addition reaction to aldehydes at rather high temperature was reported.[9] In this case, alkenyl group is substituted by two hetero atoms, and which seems to be increasing the reactivity.

(9) P. Jacob, III and H. C. Brown, J. Org. Chem., 42, 579 (1977)

(10) The ^{1}H NMR spectra of the reaction mixture involved the following data; R=Ph, δ=5.27 (d, J=9Hz), 5.75 (d, J=3Hz); R= C_5H_{11}, δ=4.56 (dt, J=6 and 8 Hz), 5.08 (d, J= 8 Hz). They support the presence of intermediate (II).

(11) As for the synthesis of the queen substance, see: (a) H. J. Bestmann, R. Kunstmann, and H. Schulz, Ann., 699, 33 (1966). (b) B. M. Trost and T. N. Salzmann, J. Org. Chem., 40, 148 (1975). (c) B. M. Trost and K. Hiroi, J. Am. Chem. Soc., 98, 4313 (1976). (d) B. M. Trost, T. N. Salzmann, and K. Hiroi, ibid., 98, 4887 (1976). (e) J. Tsuji, K. Masaoka, and T. Takahashi, Tetrahedron Lett., 18, 2267 (1977). (f) Y. Tamaru, Y. Yamada, and Z. Yoshida, ibid., 19, 919 (1978). (g) Idem., Tetrahedron, 35, 329 (1979).

(Received in Japan 19 June 1989)