CHEMISTRY LETTERS, pp. 397-400, 1975. Published by the Chemical Society of Japan

THE REACTION OF LITHIUM TRIBUTYL-1-PROPYNYLBORATE WITH OXIRANE. STEREOSELECTIVE SYNTHESIS OF (Z)- AND (E)-3-METHYL-3-OCTEN-1-OL

Kiitiro UTIMOTO, Toshiki FURUBAYASHI, and Hitosi NOZAKI

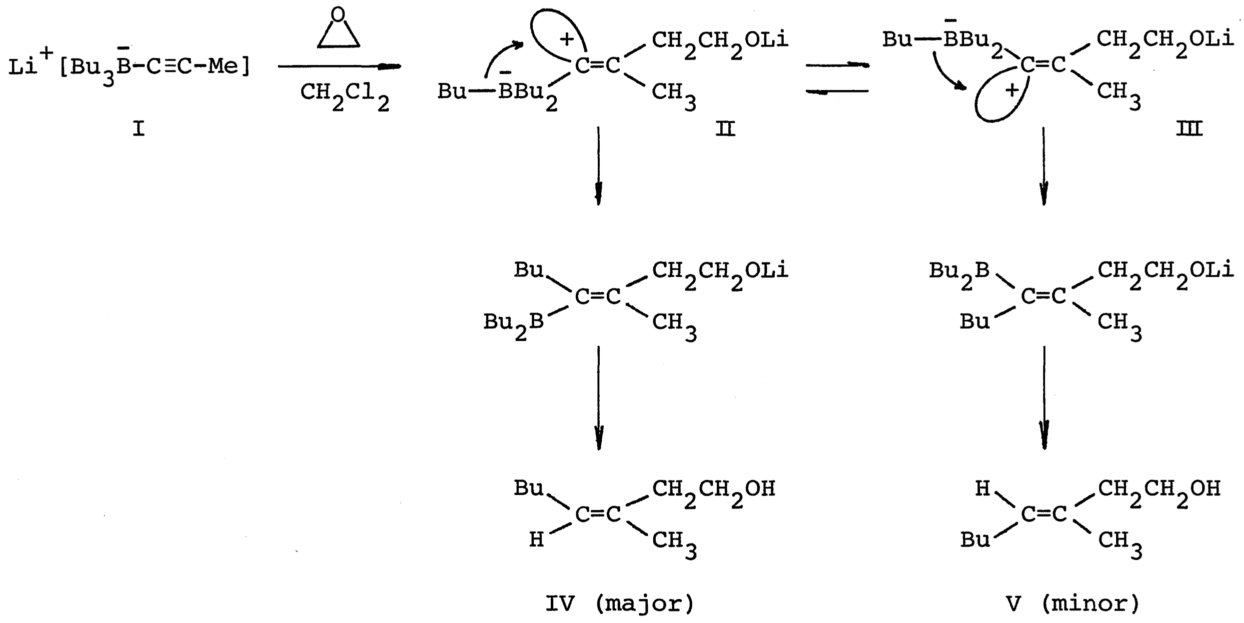
Department of Industrial Chemistry, Kyoto University, Kyoto 606

The title reaction in dichloromethane affords (Z)-3-methyl-3-octen-1-ol in good yield after the usual protonolysis, while the predominant product in THF has been found to be the (E)-isomer.

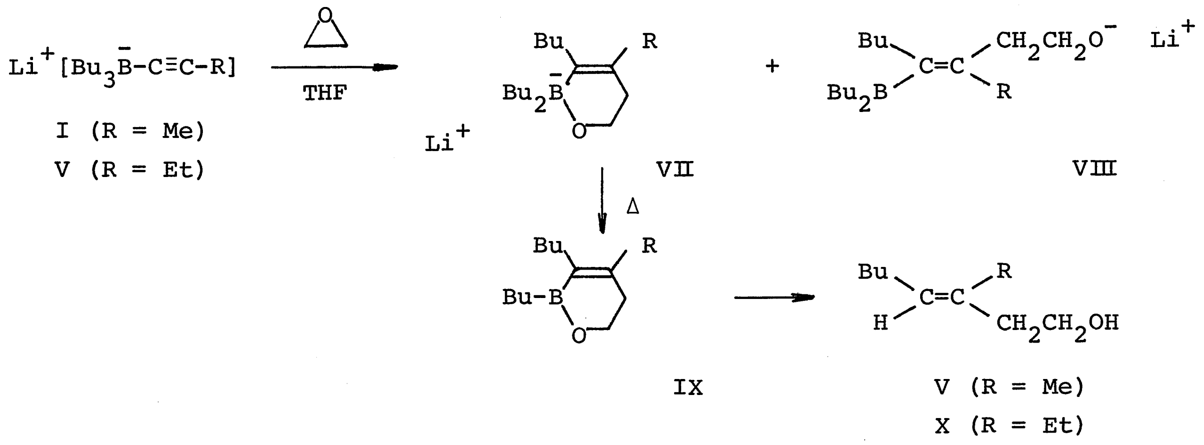
The present description of highly stereoselective procedures for the preparation of (Z)- and (E)-3-methyl-3-octen-1-ol (IV and V) by the reaction of lithium tributyl-1-propynylborate (I) with oxirane is a novel addition to the rapidly growing synthetic reactions of trialkylalkynylborates with electrophiles.[1]

To a mixture of BuLi (5 mmol in 3.75 ml of hexane solution) and propyne (5 mmol) in dichloromethane (10 ml) tributylborane (5 mmol) was added at -78°C and the mixture was stirred at room temperature for 3 hr. Oxirane (7.5 mmol) was then added at -78°C, the whole mixture was gradually heated up to room temperature and stirred overnight. Treatment with acetic acid afforded (Z)-3-methyl-3-octen-1-ol[2] (IV) in 62% yield (purity 92%). Lithium tributyl-1-butynylborate gave (Z)-3-ethyl-3-octen-1-ol with moderate stereoselectivity. Both the (Z)- and (E)-isomers were obtained in a ratio of 72:28.[3]

The observed stereoselectivity is attributed to the preferred (E) configuration of the intermediary boron inverse ylide (II)[4] which gives the predominant (Z)-isomer upon 1,2-alkyl shift with retention of configuration of the olefinic carbon.[6] Remarkably, however, the solvent-change from dichloromethane to THF has reversed the stereochemistry.[9]



To a THF-hexane (10 and 3.8 ml) solution of lithium tributyl-1-propynylborate (5 mmol) oxirane (7.5 mmol) was added at -78°C. The reaction mixture was gradually heated up to room temperature and was treated with excess acetic acid at reflux. A mixture of (Z)- and (E)-3-methyl-3-octen-1-ol (IV and V)^{10} was obtained in 72% yield (ratio 40:60). Lithium tributyl-1-butynylborate gave an analogous result [(Z)- and (E)-3-ethyl-3-octen-1-ol, 81% yield, ratio 35:65]. The postulated intermediate in THF is the (Z) conformer III, whose "naked" alkoxide ion moiety would intramolecularly interact with boron to produce the precursor VII of the (E)-olefin predominantly.^{11}

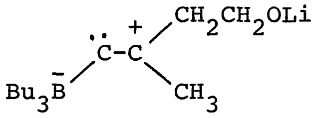


Pyrolysis of the above described reaction mixture and successive treatment with acetic acid gave exclusively (E)-products; (E)-3-methyl-3-octen-1-ol (V, yield 28%, purity 93%), (E)-3-ethyl-3-octen-1-ol (X, yield 34%, purity 98%).[12]

The above described procedure for the preparation of (Z)- and (E)-3-methyl-3-octen-1-ol, respectively, is a novel method for the preparation of trisubstituted ethylenes.

REFERENCES AND REMARKS

1. (a) A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, J. Amer. Chem. Soc., 95, 3080 (1973); (b) P. Binger and R. Köster, Synthesis, 350 (1974) and references cited therein; (c) A. Pelter, C. R. Harrison, and D. Kirkpatrick, Tetrahedron Letters, 4491 (1973); A. Pelter, K. J. Gould, and L. A. P. Kane-Maguire, J. Chem. Soc. Chem. Commun., 1029 (1974) and references cited therein; (d) M. Naruse, K. Utimoto, and H. Nozaki, Tetrahedron, 30, 3037 (1974) and references cited therein; (e) N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, Tetrahedron Letters, 2961 (1974).
2. IR (neat) ν_{O-H} 3430 cm^{-1}. NMR (CCl_4) δ ppm 0.95 (3H, t, J=7 Hz), 1.33 (4H, m), 1.74 (3H, s), 2.00 (2H, m), 2.28 (2H, t, J=7 Hz), 3.75 (2H, t, J=7 Hz), 3.75 (1H, broad), 5.20 (1H, t, J=7 Hz). Ms of the trimethylsilyl ether, m/e (rel. intensity), 214 (M^+, 1), 199 (5), 124 (17), 103 (48), 95 (18), 81 (68), 75 (21), 73 (100). Purity was determined by glc of the corresponding trimethylsilyl ether.
3. This mixture was obtained in 90% yield. Spectral data of (Z)-3-ethyl-3-octen-1-ol (purity 72%). IR (neat) ν_{O-H} 3400 cm^{-1}. NMR (CCl_4) δ ppm, in addition to alkyl protons between 0.90 and 3.00, 3.70 (1H, broad), 3.77 (2H, t, J=7 Hz), 5.15 (1H, t, J=7 Hz). Ms of the trimethylsilyl ether, m/e (rel. intensity), 228 (M^+, 1), 213 (5), 138 (13), 109 (36), 103 (50), 95 (60), 75 (23), 73 (100).
4. Stereochemistry of vinyl cations has been discussed and concluded to be in a bent form.[5] The equilibrium of two isomeric configurations (II ⇄ III) is explained by postulating such mesomeric structure as shown below.



Predominance of the configuration II is ascribed to the smaller steric requirement of the methyl group. Similar reaction mechanism was posturated by Suzuki and co-workers for the cis-olefin synthesis from trialkylalkynylborates.[1e]

5. R. H. Summerville and P. v. R. Schleyer, J. Amer. Chem. Soc., 96, 1110 (1974).
6. 1,2-Alkyl shift of the boron inverse ylide occurs with retention of configuration at the olefinic carbon. Orbital consideration[7] and parity concept[8] suggest the configurational retention is a prerequisite for that the configuration of migrating carbon is retentive.
7. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Weinheim, 1971.
8. J. Mathieu, Bull. Soc. Chim. France, 807 (1973).
9. Previously a stereoselective reaction of lithium trialkyl-1-heptynylborate with oxiranes was reported.[1d] In this case THF was used as a solvent. Stereoselectivity in the present paper is on the same line as the previously recorded.
10. (E)-3-Methyl-3-octen-1-ol (V) was obtained in high purity by the protonolysis of the pyrolysate. IR (neat) ν_{O-H} 3300 cm^{-1}. NMR (CCl_4) δ ppm 0.93 (3H, t, J=7 Hz), 1.27 (4H, m), 1.64 (3H, s), 2.00 (1H, broad), 2.10 (4H, m), 3.55 (2H, t, J=7 Hz), 5.16 (1H, t, J=7 Hz). Ms of the trimethylsilyl ether, m/e (rel. intensity), 199 (M^+-15, 5), 124 (18), 103 (50), 95 (17), 81 (60), 75 (25), 73 (100).
11. Solvent dependence of the product Z/E ratio was recorded and ascribed to intramolecular interaction of oxygen atom and borate center by Binger and Köster.[1b] Concerted mechanism giving VII can not be ruled out in the presence of a polar solvent.
12. (E)-3-Ethyl-3-octen-1-ol: IR (neat) ν_{O-H} 3330 cm^{-1}. NMR (CCl_4) δ ppm 0.97 (6H, m), 1.30 (4H, m), 2.10 (6H, m), 3.57 (2H, t, J=7 Hz), 3.75 (1H, broad), 5.15 (1H, t, J=7 Hz). Ms of the trimethylsilyl ether, m/e (rel. intensity), 228 (M^+, 1), 213 (5), 138 (10), 109 (27), 103 (63), 95 (45), 75 (25), 73 (100). The oxaborinenes IX were previously obtained by the distillation of the reaction mixtures.[1d] We have found that pyrolysis of the reaction mixture at 300°C under atmospheric pressure of argon gave the same product, whose protonolysis with acetic acid gave a pure (E)-olefin. The fate of (Z)-vinylboranes VIII is not clear.

(Received March 1, 1975)