SYNTHESIS OF (±)-ERNANDULCINE – A SWEET COMPOUND FROM *Lippia dulcis* USING BORON AND SILICON ENOLATES

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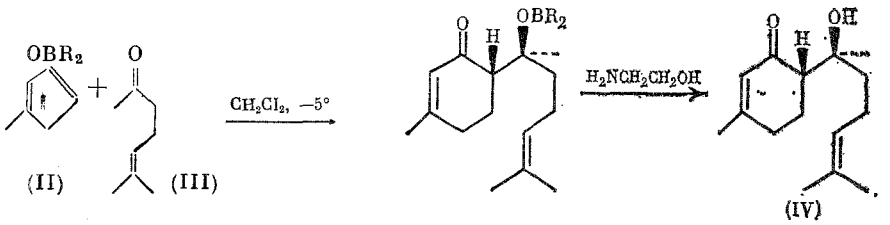
UDC 542.91:547.1'127:547.913.2

Boron and silicon ethers of enols which are readily obtained from the corresponding ketones, are very commonly used in the regio- and stereoselective synthesis of important classes of natural products [1]. The exchange reaction of $(n\text{-}C_4H_9)_2BBr$ with 3-(trimethylsilyloxy)-1-methyl-1,3-cyclohexadiene [I, mp 44-46°C (1 mm), n_D^{20} 1.4633] synthesized from 3-methyl-2-cyclohexen-1-one, was used to prepare the first dienyloxyborane, (II), which, upon condensation with ketone (III) gives (±)-ernandulcine (IV) in about 30% yield.



(II) (III) (IV)

R=*n*-C_4H_9

Product (IV) was isolated from the reaction mixture as an oil with n_D^{21} 1.4992 by the action of monoethanolamine and purified by chromatography on silica gel using hexane–ether as the eluent. IR spectrum (ν, cm^{-1}): 1643 (C=O), 3041 (CH=C), 3460 (OH). The ^1H and ^{13}C NMR and mass spectra of (IV) were in complete accord with those given in the work of Compadre et al. [2] for this compound. The sample of (IV) prepared by this method does not contain an impurity of its diastereoisomer, epiernandulcine [2].

Product (IV) was also prepared by the reaction of (I) with (III) in the presence of $TiCl_4$ in CH_2Cl_2 at from −70 to −5°C.

Ernandulcine is a bisabolene sesquiterpene which is isolated from the leaves and flowers of *Lippia dulcis* (Mexico) and is three orders of magnitude sweeter than sugar [2].

LITERATURE CITED

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2. C. M. Compadre, J. M. Pezzuto, A. D. Kinghorn, and S. K. Kamath, Science, 227, 417 (1985).

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, p. 1448, June, 1986. Original article submitted January 16, 1986.

0568-5230/86/3506-1315 $12.50