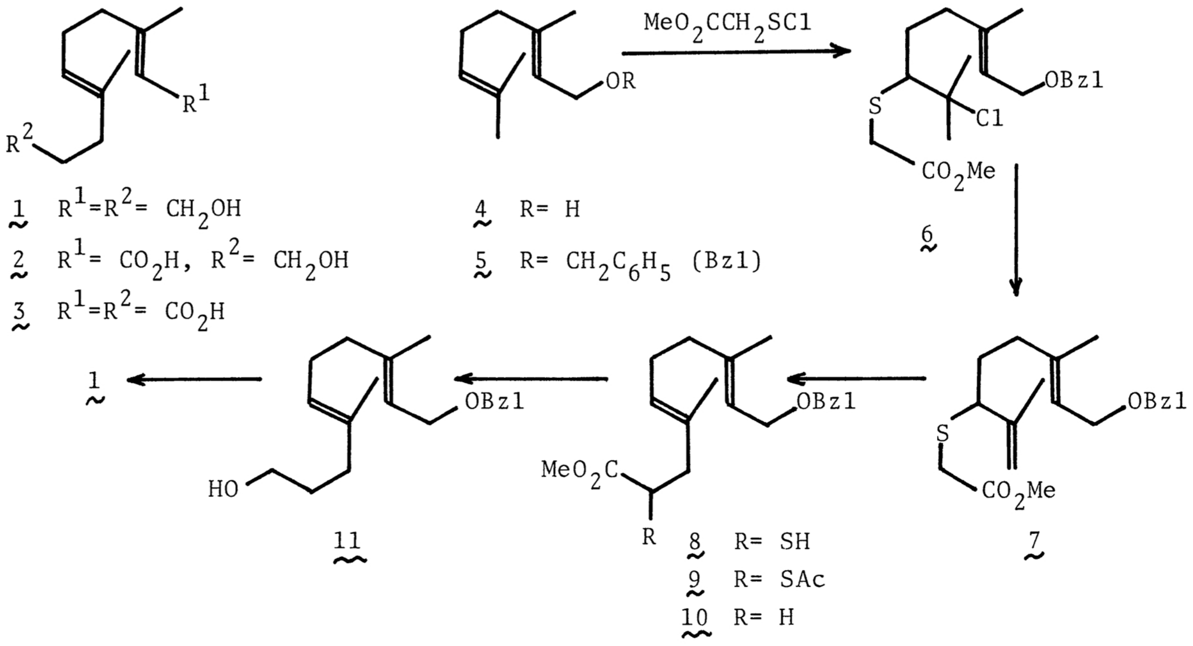
CHEMISTRY LETTERS, pp. 1061-1062, 1980. © The Chemical Society of Japan 1980

A NEW STEREOSELECTIVE SYNTHESIS OF A TERPENOID DIOL COMPONENT OF THE PHEROMONAL SECRETION OF THE QUEEN BUTTERFLY

Yukio MASAKI*, Kazuhiko SAKUMA, and Kenji KAJI
Gifu College of Pharmacy, 5-6-1 Mitahora Higashi, Gifu-Shi 502

A terpenoid diol component of the pheromonal secretion of the queen butterfly was synthesized stereoselectively from geraniol by means of a site-specific terminal olefin functionalization and the subsequent anionic [2,3]-sigmatropic rearrangement of carbomethoxymethyl allylic sulfide.

A group of pheromonal components containing a degraded sesquiterpenoid skeleton, 1, 2, and 3 have been isolated from the "hairpencils" of some species of male danaid butterflies.[1] In spite of the close structural relationship of these terpenoids with geraniol(4) the synthetic work utilizing the whole carbon skeleton of 4 has been very limited.[2] We wish to report an effective use of geraniol(4) for the synthesis of the terpenoid diol component(1) of the pheromonal secretion of the queen butterfly by the sequence depicted in which an introduction of acetic acid



moiety as the substituent on sulfur into the geraniol skeleton(5) to give an allylic sulfide(7) and the subsequent anionic [2,3]-sigmatropic rearrangement to form stereoselectively the whole carbon skeleton of the pheromone(1) are involved.

Dropwise addition of carbomethoxymethanesulfenyl chloride[3] into a solution of geranylbenzyl ether(5) in CCl_4 at 0 °C quantitatively gave an adduct(6) as a regioisomeric mixture[4] within 10 min. The crude adduct(6) was, without separation of the mixture, warmed for 20 h at 60 °C in DMF to afford regiospecifically[4] the terminal allylic sulfide(7) in 73% yield [nmr[5] 2.97(2H, s, S-CH_2-CO_2), 3.41(1H, t, S-CH(isopropenyl)-C), 4.83(2H, bs, C=CH_2)]. The anionic [2,3]-sigmatropic rearrangement smoothly proceeded by treatment of 7 with 1.2 eq of t-BuOK in THF-DMSO(1:1) at 0 °C for 2 h to lead to the α-mercaptoester(8) in 72% yield [nmr 1.90(1H, d, SH, quenched by D_2O addition), 3.17-3.16(1H, m, O_2C-CH(SH)-C)]. The structure of the α-mercaptoester(8) was also confirmed by derivatization to the acetate(9) [nmr 2.27(3H, s, $SCOCH_3$), 4.20(1H, t, O_2C-CH(SAc)-C)]. Desulfurization was carried out by treatment of 8 with the deactivated Raney-Ni[6] in acetone for 15 min at room temperature to afford the ester(10) in 82% yield [nmr 1.60(6H, s, two vinylic CH_3), 2.28(4H, bs, O_2C-CH_2CH_2-C), 3.56(3H, s, CO_2CH_3), 5.10, 5.30(each 1H, bt, two olefinic H)]. The stereoselctivity of the [2,3]-sigmatropic rearrangement was determined as 89:11 for (E):(Z) by glc and gc-ms analysis[5] of 10. The titled pheromonal diol(1) was obtained by reduction of 10 with $LiAlH_4$ in ether leading to the mono-ol(11) followed by the Birch reduction with lithium in liq.NH_3 in 68% overall yield from 10. The spectroscopic properties of the synthetic diol(1) and its diacetate are indistinguishable from those reported[1a,7] on the authentic samples except for the observation of minor contamination with its 6(Z)-isomer (11%) in glc analysis.

References and Notes

1 a) J. Meinwald, Y. C. Meinwald, and P. H. Mazzocchi, Science, 164, 1174 (1969); b) J. Meinwald, A. M. Chalmers, T. E. Pliske, and T. Eisner, Tetrahedron Lett., 1968, 4893; ibid., Chem. Commun., 1969, 86.

2 B. M. Trost, and L. Weber, J. Org. Chem., 40, 3617 (1975).

3 The reagent was prepared from methyl thioglycolate and SO_2Cl_2 in the presence of pyridine at 0 °C in CCl_4 for 40 min and used in situ without isolation.

4 Y. Masaki, K. Hashimoto, K. Sakuma, and K. Kaji, J. Chem. Soc., Chem. Commun., 1979, 855 and references cited therein.

5 NMR were measured in CCl_4 and reported in ppm from internal TMS. GLC and gc-ms were performed by using the columun packed with 2% Silicone OV-105 on Chromosorb W.

6 The freshly prepared Raney-Ni was refluxed in acetone for 15 min.

7 J. A. Katzenellenbogen, and K. J. Christy, J. Org. Chem., 39, 3315 (1974).

(Received June 11, 1980)