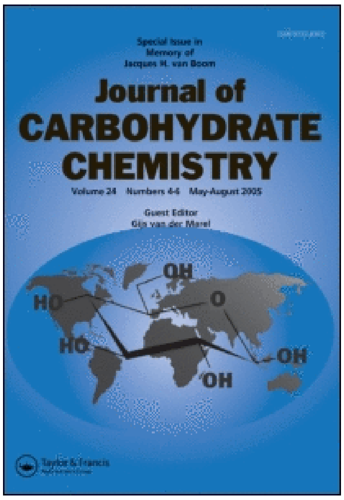

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Stereoselective Synthiesis of Both Enantiomers of Disparlure from D-Glucose

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To cite this Article Achmatowicz Jr., Osman and Sadownik, Andrzej(1985) 'Stereoselective Synthiesis of Both Enantiomers of Disparlure from D-Glucose', Journal of Carbohydrate Chemistry, 4: 3, 435 — 440

To link to this Article: DOI: 10.1080/07328308508070193

URL: http://dx.doi.org/10.1080/07328308508070193

J. CARBOHYDRATE CHEMISTRY, 4(3), 435-440 (1985)

Communication

STEREOSELECTIVE SYNTHESIS OF BOTH ENANTIOMERS OF DISPARLURE FROM D-GLUCOSE

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Received December 28, 1984 - Final Form May 1, 1985

ABSTRACT

D-Glucose was transformed stereoselectively into (7R,8S)-8-benzyloxy-7-hydroxy-2-methyl-9-octadecene from which both enantiomers of disparlure, (7R,8S)-(+)-and (7S,8R)-(-)-7,8-epoxy-2-methyloctadecane, sex pheromone of the gypsy moth, were obtained in four and three steps, respectively.

The principal sex attractant emitted by the female gypsy moth, Porthetria (Lymantria) dispar was identified as (Z)-7,8-epoxy-2-methyloctadecane and named disparlure.[1] Since then numerous syntheses of the racemic form of this pheromone have been described.[2] To establish the stereochemistry of the natural sex pheromone and to obtain an active enantiomer for field experiments several syntheses of optically active disparlure 1 and 2 have been developed.[3,4]

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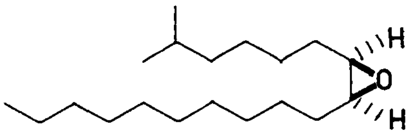

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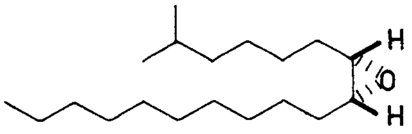
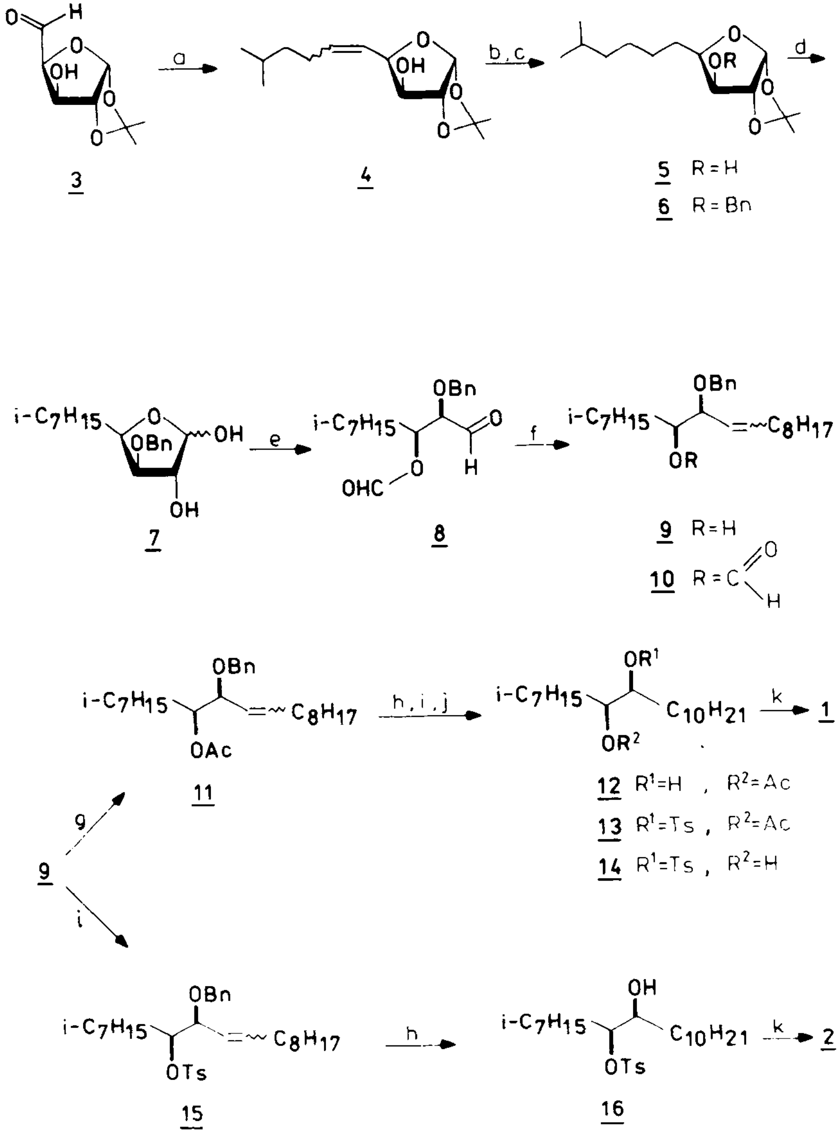


2

The strategy employed consisted in either using a suitable chiral substrate[3] or applying Sharpless asymmetric epoxidation[5] as a key step introducing the desired chirality.[4]

We wish now to report on a novel synthesis of optically active disparlure from an inexpensive chiral substrate, D-glucose. The Scheme outlines how this approach was put to practice. Wittig reaction of 1,2-O-isopropylidene-α-D-xylo-pentodialdo-1,4-furanose (3), readily available from from D-glucose[6] with ylide obtained from 1-hexyltriphenylphosphonium bromide gave, after distillation, alkene 4, bp 120-140°C/0.1 Torr as a (Z) and (E)-isomer mixture (TLC)[7]. Contaminating phosphorous compounds[8] were removed with Raney nickel and then 4 was hydrogenated to afford alcohol 5, mp 60°C, $[\alpha]^{22}$-11.8° (c 2.7; CCl_4). Benzyl ether 6, bp 152-4°/0.01 Torr, $[\alpha]^{22}$ -42.4° (c 2.4; CCl_4), obtained from 5 was hydrolyzed and the product chromatographed over a silica gel column in benzene-ethyl acetate 1:6 solution to give furanose 7, mp 46-49°C, $[A]^{22}$ -3.6° c 2.4; $CHCl_3$, after 24 h $[\alpha]^{22}$ -4.9°). Cleavage of the C_1 - C_2 bond in 7, filtration through, a Celite pad and evaporation gave unstable aldehyde 8 as a thick syrup, Wittig reaction between ylide obtained from nonyltriphenylphosphonium bromide and aldehyde 8 yielded a 1:1 mixture (TLC) of benzyloxy alcohol 9 and its formate 10. Removal of formyl group from the latter followed by chromatography on a silica


3
a
4
b, c
d
5 R=H
6 R=Bn
7
e
8
f
9 R=H
10 R=C(=O)H
11
h, i, j
12 R¹=H , R²=Ac
13 R¹=Ts , R²=Ac
14 R¹=Ts , R²=H
k
1
g
i
15
h
16
k
2

Scheme[11]

gel column in benzene solution afforded pure benzyloxy alcohol 9 as a (Z) and (E)-isomer mixture (TL). The discrimination of hydroxy groups in 9 which allowed for the synthesis of (+) and (-)-disparlure from the single chiral synthone was straightforward.

(Z) and (E)-isomer mixture (TLC) of acetate 11, bp 180°c/ 0.01 Torr, obtained from 9 was hydrogenated to give hydroxy acetate 12, which after distillation, bp 138° C/0.1 Torr, solidified, mp 28-31°C, $[\alpha]^{22}$ +18.9° (c 7.5; CCl_4). Oxirane ring closure in the tosylate 13, $[\alpha]^{22}$ +17.2° (c 2.4; CCl_4), obtained from 12, gave (7R,8S)-(+)-disparlure (1), $[\alpha]^{22}$ +0.1° (neat), bp 132°C/0.02 Torr, exhibiting all expected properties.[9] Its enantiomeric purity was examined as follows. Methanolysis of 13, followed by silica gel chromatography to remove traces of starting material gave crystalline hydroxy tosylate 14, $[\alpha]^{20}$ +15.9° (c 2.3; CCl_4),[10a] enantiomeric to the one described previously, for which enantiomeric purity (>98%) was rigorously established.[3b] Specific rotation of our sample indicated at least the same enantiomeric purity of 13 and consequently of our (+)-disparlure as that achieved by Mori et al.[3b] Changing the site of tosyloxy group to C-7 led to (-)-disparlure (2), also of high enantiomeric purity. Thus hydrogenation of tosylate 15 obtained from 9 gave hydroxy tosylate 16, mp 42-44°C, $[\alpha]^{22}$ +12.8° (c 4.5; CCl_4).[10b] Oxirane ring closure in the latter afforded (7S,8R)-(-)-disparlure (2), bp 132°C/0.02 Torr, $[\alpha]^{20}$ -0.7° (c 4.1; CCl_4).

Full experimental details and results of field tests will be published in a forthcoming paper.

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7. Satisfactory elemental analyses and spectral data (^{1}H NMR, IR) were obtained for all compounds described in this paper.

8. D. E. Plaumann, B. J. Fitzsimmons, B. M. Richtie and B. Fraser-Reid, J. Org. Chem., 47, 941 (1982).

9. Small specific rotation of disparlure renders its value a very inaccurate measure of enantiomeric purity. Unexpectedly small rotation of our sample we attribute to the poor sensitivity of the instrument at our disposal.

10. Mori et al.[3b] reported for enantiomeric hydroxy tosylate:
   (a) $[\alpha]^{23}$ -14.3° (c 2.0; $CHCl_3$);
   (b) $[\alpha]^{24}$ -12.3° (c 2.0; $CHCl_3$).

11. (a) NaH, DMSO, i-$C_6H_{13}PPh_3Br^-$, 70°C $\overset{3}{-}$ r.t., 47%;
   (b) Raney Ni/W-8, EtOH, r.t.; H_2, EtOH, 5% Pd-C, 83%;
   (c) NaH, DMSO, BnCl, 86%;
   (d) 80% CF_3CO_2H, DME, r.t., 0.5 h, 62%;
   (e) $Pb(OAc)_4$, C_6H_6, r.t., 0.5 h;
   (f) $C_9H_{19}PPh_3Br^-$, BuLi, THF, +5°C, 1 h, MeOH, r.t., 12 h, 62% (balanced on $\underline{7}$);
   (g) Ac_2O-py., 96%;
   (h) H_2, AcOH, 5% Pd-C, 98%;
   (i) TsCl-py., 93%;
   (j) 1% HCl/MeOH, r.t.;
   (k) 0.25 M KOH/MeOH, 0°C, 1 h, 85%.