Registry No. 3a, 61063-39-6; **3b**, 71031-61-3; **3c**, 71031-62-4; **4a**, 61063-43-2; **4b**, 71031-63-5; **4c**, 71031-64-6; **5a**, 19377-74-3; **5b**, 19377-70-9; **5c**, 71031-65-7; **7**, 71031-66-8; **8**, 19377-75-4; **9**, 36626-07-0; **10**, 36626-08-1.

A Convenient Stereoselective Route to the Sex Pheromone of the Red Bollworm Moth via an Allylic Sulfenate to Sulfoxide Rearrangement

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Received April 17, 1979

Among the insect pests for which a sex pheromone has been identified is the red bollworm moth, *Diparopsis castanea* Hmps., which does substantial damage to the cotton crop in southeastern Africa. The most potent of the sex pheromones produced by the virgin female of this species has been shown by Nesbitt and co-workers[1] to be (*E*)-9,11-dodecadien-1-ol acetate (**7**). Five synthetic routes to this pheromone have been reported.[2] Unfortunately, all of these methods are nonstereoselective and generally require a lengthy sequence of reactions. We wish to report a different synthetic approach which is both stereoselective and convenient for small-scale preparation of this pheromone (**7**).

In planning the route to **7**, allylic alcohol **4** (Scheme I) seemed to be the most attractive intermediate. Once synthesized, it can be treated with 2,4-dinitrobenzenesulfenyl chloride[3] in the presence of triethylamine, using a method recently developed by Reich and co-workers[4] for the 1,4-dehydration of allylic alcohols. The sulfenate ester initially formed from allylic alcohol **4** under such reaction conditions should rapidly rearrange to the corresponding allylic sulfoxide, which can subsequently undergo a syn elimination to afford conjugated diene **5**.

Allylic alcohol **4** was obtained in 55% yield by addition of crotonaldehyde (**3**)[5] to the Grignard reagent prepared from the tetrahydropyranyl ether derivative **2** of 8-bromo-1-octanol.[6] The latter compound (**1**) was in turn readily obtained in 90% yield by continuous extraction with cyclohexane of a solution of 1,8-octanediol[3] in aqueous hydrobromic acid at 75 °C. As we had anticipated, treatment of allylic alcohol **4** with an excess of 2,4-dinitrobenzenesulfenyl chloride and triethylamine at 80 °C afforded the desired conjugated diene **5** in 37% yield, after purification via column chromatography. The total synthesis was formally completed by removal of the tetrahydropyranyl blocking group to give (*E*)-9,11-dodecadien-1-ol (**6**) in approximately 18% overall yield from 1,8-octanediol. The physical and spectral properties of the latter alcohol **6** were consistent with those previously reported[7] for this same compound.

Since the *E* and *Z* stereoisomers of dienol **6** have been reported[8] to be difficult to resolve by chromatographic methods, the stereoisomeric purity of our final product was determined by subjecting dienol **6** to a previously utilized[9] procedure. The latter involved selective epoxidation of the internal double bond in **7** followed by VPC analysis of the corresponding monoepoxide. The failure to detect any of the *Z* stereoisomer indicated that the [2,3]-sigmatropic rearrangement of the sulfenate ester derived from allylic alcohol **4** proceeded stereospecifically. In view of the stereoselectivity of this process and the few steps required overall, the method reported in this note is a convenient one for synthesis of small quantities of the sex pheromone of the red bollworm moth.

Experimental Section

General. Reactions were carried out under a nitrogen atmosphere. The isolation of reaction products was accomplished by extracting them with the specified solvent. The combined extracts were washed thoroughly with 1 M aqueous sodium hydroxide solution followed by water and saturated brine and then dried over anhydrous magnesium sulfate. The solvent was removed from the dried extracts by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. Tetrahydrofuran was purified prior to use by distillation from lithium aluminum hydride. The NMR spectra were recorded with a Varian EM-360 spectrometer, and infrared spectra were obtained, using a Beckman Acculab 1 spectrophotometer. Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5750 chromatograph, using a 6 ft × 0.125 in. SE-30 column. Where indicated, percentages refer to peak areas without correction for response factors relative to an internal standard. The microanalysis was performed by Micro-Tech Laboratories, Skokie, Ill.

8-Bromo-1-octanol (1). The procedure[6] utilized by Chapman and co-workers to prepare bromide **1** was modified as follows: A mixture of 1,8-octanediol[3] (4.23 g, 28.9 mmol), 130 mL of 48% aqueous hydrobromic acid, and 40 mL of H_2O was heated at 75 °C for 72 h while being continuously extracted with cyclohexane. The product was isolated from the cyclohexane extract in the usual manner, affording 5.44 g (90%) of monobromide **1**, the physical and spectral properties of which were identical with those previously reported[6] for this same compound. VPC analysis (oven temperature 182 °C, flow 15 mL/min) indicated the product (retention time, 5.4 min) to be >98% pure.

8-Bromo-1-(tetrahydropyran-2-yloxy)octane (2). The procedure[6] utilized by Chapman and co-workers to prepare tetrahydropyranyl ether **2** was modified as follows: A solution of 1.40 g (6.69 mmol) of alcohol **1** and 1.0 mL (11.0 mmol) of 2,3-dihydropyran in 8.0 mL of anhydrous ether containing 13 mg of *p*-toluenesulfonic acid monohydrate was stirred at room temperature for 16 h. The product was recovered by dilution of this mixture with 25 mL of ether followed by the general experimental isolation procedure. Removal of the solvent followed by evaporative distillation gave 1.93 g (98%) of tetrahydropyranyl ether **2**: bp 90–100 °C (bath temperature) (0.07 mm) [lit.[6] bp 99 °C (0.02 mm)]; the NMR spectrum was identical with that previously reported[6] for this same compound.

(*E*)-12-(Tetrahydropyran-2-yloxy)-2-dodecen-4-ol (4). A 50-mL, three-necked flask was charged with Mg turnings (411 mg, 16.9 mg-atoms) and a magnetic stirring bar and dried for 2 h in an oven at 125 °C. After the mixture was cooled under nitrogen, a small crystal of iodine and approximately 10% of a solution of bromide **2** (1.30 g, 4.44 mmol) in anhydrous tetrahydrofuran (8.0 mL) were added. After initiation of the reaction, as signified by the discharge of the dark iodine color, the rest of the bromide–THF solution was added dropwise over 30 min. After this mixture was stirred at room temperature for an additional 60 min, the solution was transferred via pipet to another 50-mL,

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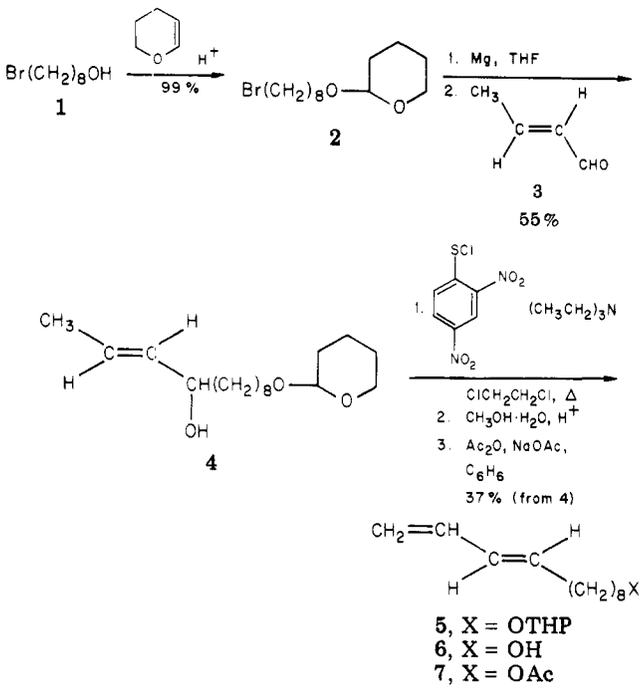
(2) Mandai, T.; Yasuda, H.; Kaito, M.; Tsuji, J.; Yamaoka, R.; Fukami, H. *Tetrahedron* **1979**, *35*, 309, and references cited therein.
(3) Available from Aldrich Chemical Co., Milwaukee, Wis.
(4) Reich, H. J.; Reich, I. L.; Wollowitz, S. *J. Am. Chem. Soc.* **1978**, *100*, 5981.
(5) NMR analysis of crotonaldehyde (purified by distillation prior to its addition to the reaction mixture) indicated the presence of only the *E* stereoisomer.
(6) 8-Bromo-1-octanol (**1**) and the corresponding tetrahydropyranyl ether (**2**) have previously been synthesized, using a similar approach. See Chapman, O. L.; Mattes, K. C.; Sheridan, R. S.; Klun, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 4878.
(7) Mori, K. *Tetrahedron* **1974**, *30*, 3807.
(8) Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *Tetrahedron Lett.* **1973**, 4669.
(9) Babler, J. H.; Martin, M. J. *J. Org. Chem.* **1977**, *42*, 1799, footnote 13.

0022-3263/79/1944-3723$01.00/0

Scheme I



three-necked flask equipped with an addition funnel charged with 312 mg (4.45 mmol) of distilled[5] crotonaldehyde (3) and 3.0 mL of anhydrous tetrahydrofuran. After the flask was cooled to 0 °C in an ice water bath, the crotonaldehyde was slowly added dropwise over 3 min. The mixture was subsequently stirred at 0 °C for 20 min before the reaction was quenched by addition of 5 mL of saturated aqueous ammonium chloride. The product was isolated in the usual manner by extraction with ether. Chromatography of the crude product mixture (1.10 g) on Florisil (50 mL, elution with hexane–15% ether), followed by evaporative distillation, afforded 692 mg (55%) of allylic alcohol 4: bp 130–145 °C (bath temperature) (0.07 mm); ν_{max} (film) 3420 (OH), 1675 (C=C), 1205, 1138, 1125, 1075, 1030, 970, 908, 870, 810 cm^{-1}; NMR δ_{Me_4Si} (CCl_4) 5.52 (m, 2 vinyl H's), 4.55 (br s, 1 H, OCHO), 3.1–4.2 (complex, 5 H, CH_2O and CHOH), 2.27 (s, OH), 1.1–2.2 (complex, 23 H). Anal. Calcd for $C_{17}H_{32}O_3$: C, 71.78; H, 11.34. Found: C, 71.55; H, 11.53.

(*E*)-12-(Tetrahydropyran-2-yloxy)-1,3-dodecadiene (5). To a solution of 278 mg (0.98 mmol) of allylic alcohol 4 and triethlyamine (0.50 mL, 3.6 mmol) in 2.0 mL of 1,2-dichloroethane was added, in small portions over a period of several minutes, 576 mg (2.46 mmol) of 2,4-dinitrobenzenesulfenyl chloride.[3] This solution was subsequently heated under gentle reflux at 80–85 °C (bath temperature) for 2 h. Dilution of this mixture at room temperature with 30 mL of 1 M aqueous sodium hydroxide solution followed by extraction with ether afforded 303 mg of crude diene 5, contaminated with a substantial amount of aromatic impurities. Chromatography on 15 mL of silica gel or Florisil (elution with hexane–2% ether) afforded 96 mg (37%) of diene 5 which previously had been prepared[7] by a Grignard coupling reaction.

(*E*)-9,11-Dodecadien-1-ol (6). Tetrahydropyranyl ether 5 (95 mg) was dissolved in 2.0 mL of methanol containing 0.10 mL of water and 3 mg of *p*-toluenesulfonic acid monohydrate. This mixture was subsequently heated at 40–45 °C (bath temperature) for 3 h, after which the product was isolated in quantitative yield by extraction with ether. VPC analysis (oven temperature, 192 °C; flow 15 mL/min; retention time, 5.5 min) indicated that dienol 6 was >99% pure. The IR and NMR spectral properties of the product were virtually identical with those previously reported[7,9] for this same alcohol (6). Subsequent analysis, using a method devised by Nesbitt and co-workers,[8,9] indicated that dienol 6 was stereochemically homogeneous.

Registry No. 1, 50816-19-8; 2, 50816-20-1; 3, 123-73-9; 4, 71342-05-7; 5, 70863-83-1; 6, 55110-79-7; 7, 50767-78-7; 1,8-octanediol, 629-41-4; 2,3-dihydropyran, 110-87-2.

Cyclodehydration Reactions Using Molten Sodium Tetrachloroaluminate[1]

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Received April 30, 1979

Intramolecular acylation of aryl-(alkyl)-carboxylic acids has been effected most commonly through the use of poly(phosphoric acid) (PPA).[2] We have found that these reactions often proceed in better yields and provide purer products, using fused sodium tetrachloroaluminate as the reagent and solvent for the cyclizations.

The use of molten salts as media for organic reactions is well established;[3] however, they have seen infrequent use in synthetic organic chemistry. Molten tetrachloroaluminates provide several advantages as organic reaction media: the reagents are inexpensive and readily available; the medium is highly selective in its reactions; and workup procedures are unusually simple and convenient. A surprisingly large number of functional groups are completely stable to the reaction conditions. For instance, the following compounds are recovered intact after treatment at 300 °C for 25 min: diphenyl ether, diphenylamine, dibenzofuran, dibenzothiophene, carbazole, acridine, phenanthridine, coumarin, and caffeine.

Table I outlines representative cyclodehydrations which are easily accomplished, using molten sodium tetrachloroaluminate. The procedures involve mixing measured quantities of NaCl and $AlCl_3$, heating them until they fuse (at about 155 °C), adding the substrates, and stirring the mixture for the appropriate contact time. After cooling the solution and hydrolysis of the salt, a simple extraction with methylene chloride normally affords products of purity similar to those available commercially.

Experimental Section[4]

General Procedure. A 1-L, round-bottom, three-neck flask was fitted with a heating mantle, mechanical stirrer, thermocouple well, and nitrogen inlet. $AlCl_3$ (50 g; 0.38 mol) (Mallinckrodt AR) and 25 g (0.43 mol) of NaCl (Baker Reagent) were added, and the mixture was stirred and heated until it had melted and its temperature had stabilized at the desired point. The starting material (about 10 g) was added, with constant stirring throughout the addition and contact period. After the appropriate contact time had elapsed, the molten mixture was poured into a 2-L beaker, which was tilted and rotated to allow the mixture to solidify as a thin layer on its sides and bottom. Decomposition of the salt with warm water (200 mL) was followed by extraction with distilled methylene chloride. Evaporation of the methylene chloride afforded the products, normally of sufficient purity (>97%) for use without further purification.[5]

1-Indanone (1). Reaction of 3-phenylpropanoic acid for 5 min at 170 °C afforded a 96% yield of 1-indanone, spectroscopically

(1) This work was supported by a Biological Research Support Grant and a Faculty Research Grant from Colorado State University and by the Laramie Energy Research Center.

(2) (a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, 58, 321 (1958); (b) E. J. Eisenbraun et al., *J. Org. Chem.*, 36, 2480 (1971); (c) G. Metz, *Synthesis*, 612, 614 (1972); (d) H. R. Synder and F. X. Werber, "Organic Synthesis", Collect. Vol. III, Wiley, New York, 1955, p 798.

(3) (a) Review: H. L. Jones and R. A. Osteryoung in "Advances in Molten Salt Chemistry", Vol, 3, Plenum Press, New York, 1975, pp 121–176; (b) D. B. Bruce, A. J. S. Sorrie, and R. H. Thomson, *J. Chem. Soc.*, 2403 (1953); (c) G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647 (1957).

(4) Melting points are uncorrected. identification and purity of all products were confirmed by spectroscopic comparison with authentic samples.

(5) The authors would like to thank Linda Stell, Kleber Hadsell, and Kurt Short for verification of procedures and yields.

0022-3263/79/1944-3724$01.00/0