(1.05 g, 7.5 mmol) and sodium bicarbonate (0.55 g, 6.5 mmol) in ethanol (50 mL) and water (10 mL) was added to a solution of 4,4-dimethoxycyclohexadienone (0.77 g, 5 mmol) in ethanol (50 mL), and the resulting mixture was heated under reflux for 1 h. Ten drops of 10% hydrochloric acid was added and the mixture was heated under reflux for 24 h; 6 N hydrochloric acid (80 mL) was then added and reflux continued for 2 h. The reaction mixture was then cooled, neutralized with sodium bicarbonate, and extracted with chloroform (3 × 150 mL). The organic extracts were dried ($MgSO_4$) and evaporated to give crude 4-methoxyaniline. This was acetylated with acetic anhydride and the crude anilide (86%) purified by chromatography and crystallization; this gave 0.46 g (56%) of pure (IR, NMR) 4-methoxyacetanilide, mp 130–132 °C.

Conversion of 4,4-Dimethoxycyclohexadienone to Ethyl 4-Methoxyphenylacetate. The lithium enolate of ethyl α-trimethylsilylacetate[12] (5.5 mmol) was prepared in THF using the procedure described by Evans[3] for the preparation of the corresponding acetamide. A solution of 4,4-dimethoxycyclohexadienone (5 mmol) in THF (3 mL) was added to the enolate solution, and the mixture was stirred at 0 °C for 5 h. It was then added to a mixture of saturated aqueous sodium bicarbonate solution (40 mL) and methylene chloride (150 mL) which had been prechilled to 0 °C. The organic layer was separated, washed with 5% aqueous sodium chloride solution (40 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude quinone methide ketal (1.10 g) was catalytically hydrogenated (5% Pd/charcoal) at atmospheric pressure in ethyl acetate and the product chromatographed on silica gel using methanol/methylene chloride (3:97) as eluent. This gave 0.22 g of 4-methoxyphenol and 0.43 g (68% based on dienone consumed) of pure (IR, NMR, GLC) ethyl 4-methoxyphenylacetate.

Registry No.—**1**, 935-50-2; **2a**, 2396-60-3; **2b**, 29418-44-8; **2c**, 51640-06-3; $ArNHNH_2$ (Ar = Ph), 100-63-0; $ArNHNH_2$ (Ar = 4-$CH_3C_6H_4$), 539-44-6; $ArNHNH_2$ (Ar = 2,4-$(NO_2)_2C_6H_3$), 119-26-6; TTN, 13746-98-0; 3,4-dimethylphenol, 95-65-8; 3,4-dimethylazobenzene, 67425-70-1; acethydrazide, 1068-57-1; anisole, 100-66-3; 6-hydroxytetralin, 1125-78-6; tetralin, 119-64-2; hydroxylamine hydrochloride, 5470-11-1; 4-nitrosoanisole, 100-17-4; 4-methoxyacetanilide, 51-66-1; ethyl glycinate hydrochloride, 623-33-6; 4-methoxyaniline, 104-94-9; ethyl 2-trimethylsilylacetate lithium enolate, 54886-62-3; 4-methoxyphenol, 150-76-5; ethyl 4-methoxyphenylacetate, 14062-18-1.

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(9) Mp's were determined using a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer Model 467 grating infrared spectrophotometer, and NMR spectra using a Varian A-60 60 MHz spectrometer. GLC was performed on an F and M Model 810R-29 S/N B-273 gas chromatograph equipped with a Honeywell Electronik 15 strip chart recorder. TLC refers to the use of Baker-flex silica gel 1B2-F thin-layer chromatography sheets. Microanalyses were performed by Hoffmann-La Roche, Inc., Nutley, N.J.
(10) When 4-methoxyphenol is used as the substrate the reaction temperature should be held at 0 °C both before the addition of the hydroxylamine and for 1 h afterwards to prevent acid-catalyzed decomposition of the quinone ketal.
(11) Azoxyarenes are produced as by-products in small amounts in these reactions and are difficult to separate from the desired nitroso compounds. Addition of boron trifluoride eliminates this problem.
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Eutectic Potassium–Sodium–Aluminum Chloride as a Mild Catalyst for Ene Reactions: Simple Synthesis of the Sex Pheromone from Douglas Fir Tussock Moth

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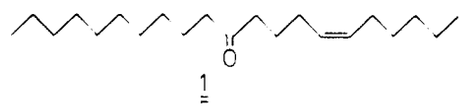
Received March 13, 1978

Several syntheses of the sex pheromone of the Douglas fir tussock moth (**1**) have recently been published.[1-4] These



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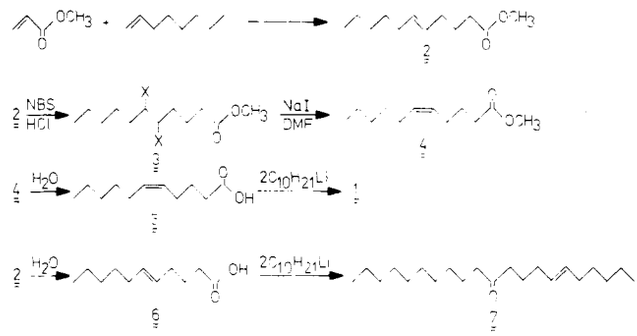
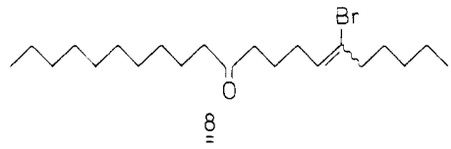
syntheses make use of fairly complicated reactions and sophisticated starting materials. During our studies of acid-catalyzed ene reactions, we have explored a simpler synthesis both for the natural isomer and the also active[5] *E* isomer (**7**). The principles of this synthesis are outlined in Scheme I.

Scheme I



The ene reaction between methyl acrylate and 1-octene has been reported not to occur with aluminium chloride.[6] This is probably due to isomerization of the 1-octene to other internally substituted octenes and subsequent formation of branched adducts. In contrast to this, the eutectic mixture of $AlCl_3$, NaCl, and KCl has been found to be a superior catalyst for the reactions of methyl acrylate with 1-olefins. Using this catalyst, a 40% yield of ene adducts was obtained as a 94:6 mixture of normal and branched isomers. Careful GC analysis (see Experimental Section) showed that the ratio of **2**/**4** was 86:14. After hydrolysis of the product mixture and reaction with decyllithium,[7] the *E* isomer **7** can be obtained by recrystallization. The conversion of the acid mixture to **5** could not be carried out satisfactorily via the straightforward bromination–dehydrobromination[8]–hydrogenation[9] reaction sequence. The overall yields were low, and the presence of **8**,



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in the product mixture, from the reaction with decyllithium indicated the interference of the carboxylate group somewhere in the bromination–dehydrobromination sequence.

Inversion of the **2**/**4** ratio could, however, be carried out very smoothly by conversion of the ester mixture to the corresponding vicinal bromochloride[10] and subsequent elimination[11] to form the inverted olefin. GC analysis showed that the inversion is not 100% stereospecific in this case since the ratio **2**/**4** of the inverted mixture was 20:80. Hydrolysis and reaction

with decyllithium then yields the pheromone.

These results show that the synthetic scope of the ene reaction of acrylate can be considerably extended by this modified Lewis acid catalyst.

Experimental Section

GC analysis was performed on a Hewlett-Packard 402 gas chromatograph with a column packed with 5% FFAP on Chromosorb W at 150–170 °C. The branched ketones were separated from the straight chain ketones on a 3.8% UCW 98 on Chromosorb W column at 240 °C. The isomers **2** and **4** were separated on a PYE GCV apparatus equipped with a CW20M 50 m SCOT column. IR spectra were recorded with Perkin-Elmer 237 and 257 instruments. NMR spectra were obtained in CCl_4 using a Varian EM 360 spectrometer with tetramethylsilane as an internal standard. Melting points were recorded on a hot stage and are uncorrected. All yields are based on isolated products.

Ene Reaction between 1-Octene and Methyl Acrylate. $AlCl_3$ (5.85 g), KCl (0.848 g), and NaCl (0.803 g) were heated while well protected from moisture in a tube of Pyrex glass until a clear solution was obtained. After cooling to room temperature, the glass tube was placed in an acetone–CO_2 bath and 40 mL of methyl acrylate, 17 mL of 1-octene, and a few crystals of hydroquinone were added. When the contents had reached −78 °C, the tube was sealed by melting and put in a boiling water bath for 16 h. The workup procedure consisted of pouring the mixture on ice and dilute hydrochloric acid, extraction with ether, washing of the ether phase, and drying. Evaporation of the solvent and distillation afforded 8.6 g (40%) of 5-hendecenoic acid methyl ester: **2**/**4** ratio was 86:14; IR showed strong absorption at 970 cm^{-1}, suggesting mainly the *E* isomer; NMR δ 5.4–5.15 (m, 2 H), 3.55 (s, 3 H), 2.35–0.80 (m, 17 H), and distorted triplets centered at δ 2.15 and 0.9 corresponding to the allylic CH_2 (s) and the CH_3 at the end of the chain were observed; MS *m/e* 198 ($M^{+\cdot}$), 166 ($M - CH_3OH)^{+\cdot}$, 124 ($C_5H_4CH{=}CHCH{=}CH_2^{+\cdot}$) (McLafferty), 74 ($CH_3O{-}C(OH){-}CH_2^{+\cdot}$) (McLafferty).

Vicinal Bromochloro Ester 3. **2** (1.1 g, 5.55 mmol) was dissolved in 11 mL of CH_2Cl_2, and the solution was cooled to −78 °C in an acetone–CO_2 bath during saturation with HCl gas. Then 1.04 g of *N*-bromosuccinimide, which had been crystallized from water, was added in one portion. The temperature was then allowed to rise to −20 °C, maintaining HCl saturation. After 0.5 h at −20 °C, the mixture was poured on ice–$NaHSO_3$, extracted three times with ether, washed with $KHCO_3$ solution and water, and finally dried. Evaporation of the solvent gave 1.6 g of a colorless oil in 92% crude yield. GLC analysis of the product, which was not purified, showed that it was 93% pure. No olefin remained. IR 1740 cm^{-1} (CO); NMR δ 4.2–3.9 (broad unresolvable multiplet, 2 H), 3.67 (s, 3 H), 2.5–0.8 (m, 17 H). The NMR spectrum was very similar to the spectrum of **2**.

Formation of the Inverted Olefinic Ester Mixture. The product from the above reaction, 1.6 g, was dissolved in 60 mL of dry DMF, and 15 g of NaI was added with stirring. The temperature was then raised to 110–115 °C. After 4 h at this temperature, the mixture was poured out in H_2O and the water–DMF solution was extracted three times with light petroleum. The petroleum phase was then washed with $NaHSO_3$ solution and water and dried with magnesium sulfate. Evaporation of the solvent gave 0.99 g (99%) of a product that contained less than 1% of the bromochloro ester: **2**/**4** ratio was 20:80; IR showed weak absorption at 970 cm^{-1}, attributable to the *E* isomer present; NMR and mass spectra were practically identical with the spectra of the trans compound.

Ester Hydrolysis. The ester (0.81 g) was hydrolyzed in 5 mL of H_2O and 2 mL of EtOH with 0.3 g of KOH for 16 h at room temperature with occasional heating on a water bath at the beginning of the reaction. The usual workup procedure gave 0.77 g (95%) of acid as a colorless oil: IR showed typical broad carboxylic acid bonds at 3000–2000 cm^{-1}; NMR spectrum was similar to the NMR spectrum of the ester, except for the disappearance of the O–CH_3 and the appearance of a COOH proton at δ 11.05.

(*Z*)-6-Heneicosen-11-one (1). To 150 mg of lithium powder in 10 mL of ether was added 2.2 g of decylbromide in 3 mL of ether during 1 h at −10 to −15 °C. After additional stirring for 2 h, GLC analysis after hydrolysis of a sample showed only decane.

This decyllithium solution was then added dropwise at 0 °C with vigorous stirring to a solution of the acid in 10 mL of THF. The mixture was stirred for 16 h at room temperature and refluxed for 0.5 h. The solution was then slowly added to 100 mL of water with vigorous stirring. Extraction of the water phase three times with ether, washing, drying with magnesium sulfate, and evaporation of the ether and the majority of the decane gave 1.4 g of product. Acidification of the water phase and extraction with ether afforded 0.12 g of acid. GC analysis of the ketone revealed the existence of about 3.9% of the branched isomer. This product (0.8 g) was then chromatographed on SiO_2 with 10% ether in light petroleum as eluant. A slight enrichment could be achieved; 0.46 g of ketone was obtained, the GC analysis of which showed 2.5% of the branched isomer. This corresponds to a yield of 62% based on the acid and 75% based on consumed acid.

The *E* and *Z* ketones **7** and **1** could not be satisfactorily separated on any column tried, including the SCOT column. The *E*/*Z* ratio should, however, be 20:80 since neither the hydrolysis nor the reaction with decyllithium concerns the double bond: IR 1720 cm^{-1} (CO) and weak absorption at 970 cm^{-1}; NMR δ 5.25 (m, 2 H), 2.2 (t, 4 H), 1.9 (m, 4 H), 1.8–1.1 (m, 24 H), 1.1–0.8 (overlapping distorted triplets, 6 H); MS (70 eV) *m/e* 308 ($M^{+\cdot}$), 197 ($C_{10}H_{21}CO{-}C_2H_4^{+\cdot}$), 169 ($C_{10}H_{21}CO^{+\cdot}$), 124 ($C_5H_4CH{=}CHCH{=}CH_2^{+\cdot}$) (McLafferty).

(*E*)-6-Heneicosen-11-one (7). By hydrolyzing the ester mixture obtained in the ene reaction, the *E* ketone was synthesized the same way as described above. From 1.84 g (10 mmol) of acid there was obtained after recrystallization from ethanol 1.7 g of **7**: 55% yield based on total acid and 73% yield based on not recovered acid (0.45 g of acid could be recovered); mp 36 °C; IR showed strong absorption at 970 cm^{-1} (trans double bond); NMR and mass spectra were practically identical with the spectra of the cis compound.

Registry No.—**1**, 54844-65-4; **2**, 67270-84-2; **3**, 67254-48-2; **4**, 54471-23-7; **6**, 67270-85-3; **7**, 54844-66-5; methyl acrylate, 96-33-3; 1-octene, 111-66-0; decyl bromide, 112-29-8; $AlCl_3$, 7446-70-0; NaCl, 7647-14-5; KCl, 7447-40-7.

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Stereochemical Control of Transpositional Allylic Oxidation[1,2]

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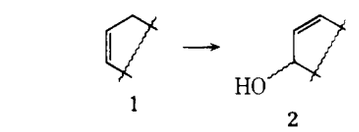
Received April 4, 1978

The facility of transpositional allylic oxidation (eq 1) was greatly increased by the discovery by Reich,[4] and also Sharpless[5a] and Clive,[5b] that PhSeX could be utilized for effecting the process. Based on ^1H NMR spectra of intermediates of type **3**, Reich[4] concluded that the PhSeOAc addition to **1** oc-



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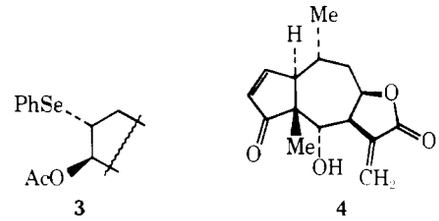

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