through the 4,6-O-benzylidene-D-glucopyranose acylation, deblocking route. H. G. Fletcher, Jr., *ibid.*, 231 (1963).
(4) A similar anionic equilibration has recently been observed for glucose: G. deWit, A. P. G. Kiekoom, and H. vanBekkum, *Tetrahedron Lett.*, 3943 (1975).
(5) The composition of TBG, e.g., the commercially available mp 149–150 °C material, in both benzene and THF has been determined by 220-MHz ^{1}H NMR to be approximately a 60:40 mixture of α and β anomeric forms. This ratio appears to remain approximately the same in the temperature range 17–56 °C.
(6) Note that addition of 4% HMPA to benzene v/v increases the solvating power of the medium enough to reverse the α:β product ratio to 2.3:1.
(7) O. T. Schmidt and J. Herok, *Justus Liebigs Ann. Chem.*, **587**, 63 (1954).
(8) C. Pedersen and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **82**, 3215 (1960).
(9) H. B. Wood, Jr., and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **78**, 2849 (1956).
(10) Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

A Synthesis of (*Z*)-6-Heneicosen-11-one. The Sex Pheromone of the Douglas Fir Tussock Moth[1]

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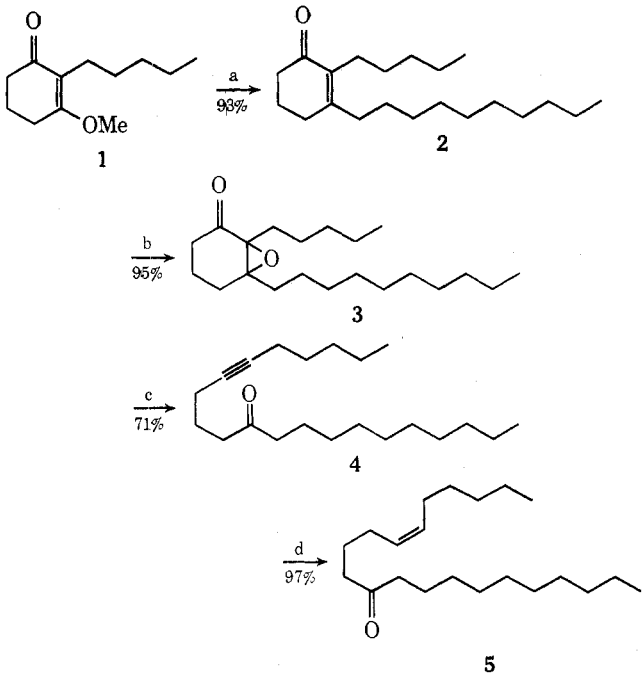
The sex pheromone of the Douglas fir tussock moth *Orgyia pseudotsugata* (McDunnough) has recently been identified as (*Z*)-6-heneicosen-11-one (**5**),[2] which is unusual in that most lepidopterous sex pheromones thus far identified are monoene or diene fatty alcohols or acetates of C_{12} or C_{14} chain length.[3] The structure and stereochemistry of **5** have been corroborated by unambiguous total synthesis.[4] The Douglas fir tussock moth is a severe defoliator of fir forests in western North America; consequently, considerable interest attends the use of the sex pheromone for purposes of bioassay and population control. Since traps baited with synthetic **5** have been shown to be highly attractive to males in field tests,[2] we have explored an alternate synthesis of **5** which is presented in the scheme below.

The high stereoselectivity and chemical yield anticipated for the reduction of an acetylenic bond to the corresponding *Z* olefin suggested 6-heneicosyn-11-one (**4**) as the primary synthetic goal.[5] The 21-carbon chain with the requisite 1,5 relationship between the ketone and acetylene functions in **4** was introduced in one step by the Eschenmoser cleavage[6] of the epoxy ketone **3** in 71% yield. The synthesis of the epoxy ketone **3** was achieved in two steps from the enol ether **1**[7] as shown in the scheme.



a, n-$C_{10}H_{21}MgBr/Et_2O$, H_3O^+; b, H_2O_2–NaOH/MeOH; c, p-$TsNHNH_2/CH_2Cl_2$–HOAc; d, H_2–$Pd/BaSO_4$, MeOH–pyridine.

To complete the synthesis, the acetylenic bond of **4** was semihydrogenated over Lindlar catalyst poisoned with 5 equiv of pyridine to give the *Z* olefin **5** in 97% yield (60% overall from **1**). The MS, ir, and NMR spectra of synthetic **5** were in complete accord with the published data for the natural pheromone.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer as ~5% solutions in CCl_4; NMR spectra were obtained with a Varian HA-100 instrument in CCl_4 solution using Me_4Si as an internal standard. Mass spectra were obtained on a Du Pont 29-491B spectrometer. All yields are based on pure, isolated products.

2-*n*-Pentyl-3-*n*-decylcyclohex-2-en-1-one (2). A solution of *n*-decylmagnesium bromide was prepared from 1.77 g (8.00 mmol) of *n*-decyl bromide and 0.19 g (8.25 g-atoms) of Mg in 35 ml of ether. To the magnetically stirred Grignard reagent was added dropwise 1.00 g (5.10 mmol) of 2-*n*-pentyl-3-methoxycyclohex-2-en-1-one (**1**) in 5.0 ml of ether at 0 °C. After addition was complete, the mixture was stirred at 0 °C for 30 min and at ambient temperature for 3 h. The reaction mixture was poured into 15 ml of iced 1 N HCl and the ether layer separated, washed with 2 × 10 ml of saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo to a pale yellow oil. Kugelrohr distillation afforded 1.40 g (93%) of pure **2** as a colorless oil which crystallized on refrigeration: bp 125 °C (bath, 0.18 mm); ir (CCl_4) 1665, 1618 cm^{-1}; NMR (CCl_4) δ 2.1–2.4 (m, 6 H), 1.8–2.1 (m, 2 H), 1.1–1.8 (m, 24 H), 0.8–1.1 (overlapping distorted triplets, 6 H); mass spectrum (70 eV) *m/e* 306 (60, M^+), 165 [100, $(M - C_{10}H_{21})\cdot^+$]; uv (95% EtOH) 245 nm (ϵ 17 200).

2-*n*-Pentyl-3-*n*-decyl-2,3-epoxycyclohexan-1-one (3). To a solution of 0.590 g (1.93 mmol) of enone **2** in 14 ml of MeOH was added 1.00 ml (11.6 mmol) of 30% H_2O_2 and 0.15 ml of 6 N NaOH. The reaction mixture was allowed to stir at ambient temperature for 24 h after which the MeOH solution was diluted with 35 ml of H_2O and extracted with 2 × 15 ml of ether. The combined ether layers were washed with 2 × 10 ml of H_2O, dried over $MgSO_4$, and concentrated in vacuo to a colorless oil which was distilled via Kugelrohr to afford 0.588 g (95%) of the epoxy ketone **3**: bp 120 °C (bath, 0.15 mm); ir (CCl_4) 1710 cm^{-1}; NMR (CCl_4) δ 1.8–2.2 (m, 2 H), 1.1–1.8 (m, 30 H), 0.9 (overlapping distorted triplets, 6 H).

6-Heneicosyn-11-one (4).[4] To a magnetically stirred solution of 0.588 g (1.83 mmol) of the epoxy ketone **3** in 4.0 ml of CH_2Cl_2 and 2.0 ml of HOAc at 0 °C was added 0.340 g (1.83 mmol) of *p*-toluenesulfonylhydrazide in one portion. After stirring at 0 °C for 3 h followed by 3 h at ambient temperature, the mixture was poured into 10 ml of water and extracted with 3 × 10 ml of hexane. The combined hexane layers were washed with 3 × 5 ml of water followed by 5 ml of saturated $NaHCO_3$. The mixture was dried over $MgSO_4$ and concentrated in vacuo to give 0.512 g of a pale yellow oil which consisted of two products by TLC on silica gel ($CHCl_3$ eluent, phosphomolybdic acid development). The major component, the desired acetylenic ketone **4** (R_f 0.6), was separated from a single major contaminant of unidentified structure (R_f 0.5) by column chromatography on 15 g of silica gel packed in hexane. The desired product was eluted with 5% ether in hexane to give 0.396 g (71%) of **4** as a colorless oil after distillation via Kugelrohr [bp 125 °C (bath) at 0.35 mm]. The product crystallized on standing: mp 26–27 °C; ir (CCl_4) 1718 cm^{-1}; NMR (CCl_4) δ 2.00–2.20 (m, 4 H), 1.1–1.8 (m, 24 H), 0.8–1.1 (overlapping distorted triplets, 6 H); mass spectrum (70 eV) *m/e* 306 (100, $M\cdot^+$), 169 [74 $(M - C_{10}H_{17})\cdot^+$], 165 [20, $(M - C_{10}H_{21})\cdot^+$], 122 [42, $(C_5H_{11}C{\equiv}C{-}CH{=}CH_2)\cdot^+$].

(*Z*)-6-Heneicosen-11-one (5). A solution of 0.361 g (1.18 mmol) of the acetylene **4** in 5 ml of MeOH containing 100 μl of pyridine was stirred under a slight positive pressure of H_2 over 35 mg of 5% Pd on $BaSO_4$. The progress of the reduction was followed by TLC on silica gel (5% ether in hexane as eluent, phosphomolybdic acid development). When the reaction was complete (~1 h) the catalyst was removed by filtration and the product (0.353 g, 97%) isolated via Kugelrohr distillation as a colorless oil which crystallized on refrigeration: bp 118 °C (bath, 0.4 mm); ir (CCl_4) 1718 cm^{-1}; NMR (CCl_4) δ 5.1–5.5 (m, 2 H), 2.3 (t, 4 H), 1.8–2.2 (m, 4 H), 1.1–1.8 (m, 24 H), 0.8–1.1 (overlapping distorted triplets, 6 H); mass spectrum (70 eV) *m/e* 308

(5, $M^{\cdot+}$), 167 (23, $C_{10}H_{19}C{\equiv}O^{\cdot+}$), 124 [100, $(C_5H_{11}CH{=}CHCH{=}CH_2{-})^{\cdot+}$].

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Registry No.—**1**, 59434-06-9; **2**, 59434-07-0; **3**, 59434-08-1; **4**, 54844-69-8; **5**, 54844-65-4; *n*-decyl bromide, 112-29-8.

References and Notes

(1) Part 2 of a series on pheromone synthesis. For part 1 see P. J. Kocienski and R. W. Ostrow, *J. Org. Chem.*, **41**, 398 (1976).
(2) R. G. Smith, G. E. Daterman, and G. D. Daves, *Science*, **188**, 63 (1975).
(3) K. Eiter, *Fortschr. Chem. Org. Naturst.*, **28**, 204 (1970); M. Jacobson, "Insect Sex Pheromones", Academic Press, New York, N.Y., 1972; J. G. McConnell and R. M. Silverstein, *Angew. Chem., Int. Ed. Engl.*, **12**, 644 (1973); D. A. Evans and C. L. Green, *Chem. Soc. Rev.*, **2**, 75 (1973).
(4) R. G. Smith, G. D. Daves, and G. E. Daterman, *J. Org. Chem.*, **40**, 1593 (1975).
(5) A more practical reason for choosing **4** as a key intermediate is the fact that reduction to the *E* olefin using Na/NH_3 is more amenable to large scale synthesis than alternative procedures for effecting reduction to the *Z* olefin. Smith and co-workers (see ref 2) have shown that the *E* isomer is also highly attractive.
(6) R. K. Miller, D. Felix, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 1479 (1970), and references cited therein.
(7) The enol ether **1** was prepared by reaction of 2-*n*-pentylcyclohexane-1-3-dione [K. W. Rosenmund and H. Bach, *Chem. Ber.*, **94**, 2394 (1961)] with MeOH–H_2SO_4: ir (CCl_4) 1655, 1620 cm^{-1}; NMR (CCl_4) δ 3.8 (s, 3 H), 2.55 (t, 2 H), 1.7–2.3 (m, 6 H), 1.25 (br, 6 H), 0.9 (distorted t, 3 H).

Hydrogenation of Cyclic Unsaturated Oxyphosphoranes. A Novel Method for Reduction of α Diketones to Ketones

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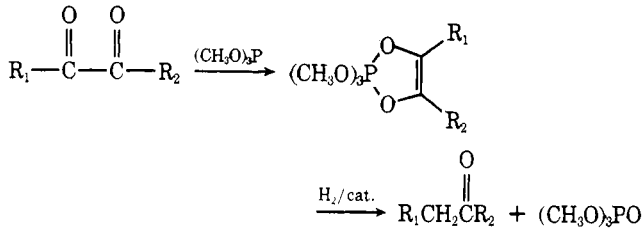
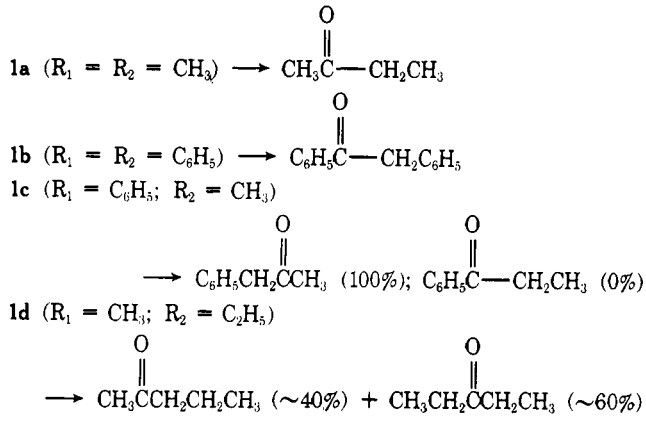
We wish to report that catalytic hydrogenation of unsaturated oxyphosphoranes such as **1** leads directly to high yields of phosphate and monoketone. Cycloadducts are obtained conveniently from diketones and phosphites.[1] Since diketones



are, in turn, available from simple monoketones, the reaction sequence shown above represents a potential solution of a difficult synthetic problem, that of ketone transposition. The procedure also offers an alternative to standard procedures for converting acyloin condensation products to monoketones.

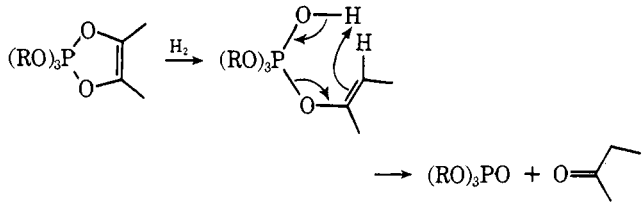
Uptake of hydrogen and yields of ketone are essentially quantitative in this reaction. Where both electronic and steric factors are contributing (example **1c**) high selectivity toward a single product is shown. In example **1d** where much lower discrimination would be expected, only a slight preference for reduction at the less hindered site is found.

This reaction appears to have little precedence in the literature. Indeed, we initiated the study with the intention of designing a method for producing stereochemically pure



erythro 1,2-diols. Alternate syntheses of the cyclic *saturated* oxyphosphoranes[3] expected from **1a** confirmed that these compounds were stable at room temperature, and, further, could be recovered unchanged after prolonged treatment under catalytic hydrogenation conditions. Therefore the saturated compound evidently does not intervene in the process to produce ketone. In earlier work it had been demonstrated by Denney[4] et al. that these cyclic saturated compounds decompose (above 100 °C) and generally yield epoxides as predominant products.

Several mechanistic rationalizations of this reaction which do not involve double bond hydrogenation may be envisaged, but they are highly speculative at this time. A simple possibility involves hydrogenolysis of the vinyl carbon–oxygen



bond, followed by the 1,5 hydrogen shift shown above. Such hydrogenolysis is documented for vinyl[5] and phenyl[6] *phosphates*, and provides precedence for the present proposal.

Experimental Section

Diketones. All diketones were available from Aldrich Chemical Co. and were purified by distillation or crystallization. Selenium dioxide oxidation of propiophenone was also employed to obtain 1-phenyl-1,2-propanedione in 60% yield.[7]

Trimethyl phosphite was distilled before each use.

Cyclic unsaturated oxyphosphoranes (1a–d) were prepared by mixing molar equivalents of trimethyl phosphite and diketone at room temperature as described by Ramirez and Desai.[1] These products were distilled or crystallized before use: **1a**, bp 36 °C (0.5 mm); **1b**, mp 48–50 °C; **1c**, bp 116–119 °C (0.9 mm); **1d**, bp 85–88 ° (10 mm).

Hydrogenations were accomplished at 1 atm H_2 over reduced PtO_2. Cyclohexane, ethyl acetate, or benzene, 5–10% in oxyphosphorane, were used as solvents. The samples typically absorb 1 molar equiv of H_2 within 2–6 h,[8] at which time H_2 uptake had slowed substantially. Hydrogenation was terminated at this point. The reaction mixtures were filtered to remove catalyst. In the case of **1a** NMR examination showed only 2-butanone and trimethyl phosphate from **1a**; **1d** showed 2- and 3-pentanone plus trimethyl phosphate. These products and product ratios were further quantified by VPC analysis. The yields were quantitative with no other products detectable. Similar analyses were performed for the products from **1b** and **1c**. The products could also be isolated by column chromatography over silica gel with ether eluent.

Saturated oxyphosphoranes were prepared from both *meso*- and *dl*-2,3-butanediol by exchange of these diols with pentaethoxyphosphorane. These procedures are described by Denney and Jones.[3] These saturated compounds could be recovered unchanged after prolonged exposure to H_2/Pt in ethyl acetate or cyclohexane.

Acknowledgment. The authors acknowledge helpful dis-