(16): IR (neat) 1632 (m), 908 (s), 751 (s) cm^{-1}; ^1H NMR δ 7.2–7.05 (m, 8 H), 6.0–5.5 (m, 1 H), 5.1–4.8 (m, 2 H), 3.96 (t, J = 7.5 Hz, 1 H), 3.86 (t, J = 7.5 Hz, 1 H), 2.53 (t, J = 7.0, 2 H), 1.4–1.1 (m, 6 H), 0.88 (t, J = 7.1 Hz, 3 H). Anal.: C, H. Identical material was obtained by addition of *n*-BuLi to anthracene followed by anion trapping with allyl bromide.

Deuterated Precursors. Monodeuterio bromide **15**-*d* was prepared by the sequence shown in Scheme V. The aldehyde **19** was obtained via oxalyl chloride–dimethyl sulfoxide oxidation[18] of perprotio alcohol **20**. The aldehyde **19** exhibited the following properties: mp 72–74 °C; IR (Nujol) 2700 (m), 1710 (s) cm^{-1}; ^1H NMR δ 9.39 (d, J = 1.7 Hz, 1 H), 7.32–7.00 (m, 8 H), 4.67 (d, J = 2.50 Hz, 1 H), 4.39 (t, J = 2.70 Hz, 1 H), 2.75 (m, 1 H), 2.09 (m, 1 H), 1.97 (m, 1 H). Anal.: C, H.

Reduction of 5.00 g (21.40 mmol) **19** with 0.498 g (11.91 mmol) of sodium tetradeuteroborate in 50 mL of ethanol at room temperature afforded **20**-*d*: 98% yield; mp 101–103 °C; IR (Nujol) 3400 (br), 2130 (w, C–D) cm^{-1}; HRMS, m/e 237.1259 (M^+; calcd for $C_{17}H_{15}DO$ 237.1264). The ^1H NMR spectrum ($CDCl_3$, 360 MHz) of **20**-*d* showed inter alia two doublets in the methylene region: δ 3.29 (J = 6.05 Hz) and 2.94 (J = 9.46 Hz), respectively (1 H).

Deuterio alcohol **20**-*d* was converted to bromide **15**-*d* in 84% yield by heating a mixture of 3.555 g (15 mmol) of **20**-*d* and triphenylphosphine dibromide [from triphenylphosphine (3.93 g, 15 mmol) and bromine (0.768 mL, 15 mmol)] in 40 mL of acetonitrile at reflux for 4 h. When the mixture cooled, bromide **15**-*d* separated as white needles; yield 3.78 g (84%) in three crops: mp 125–127 °C; ^1H NMR (inter alia) δ 3.05 (d, J = 6.21 Hz), 2.77 (d, J = 9.86 Hz), in a ratio of 1.00:2.14 (±0.05); HRMS 299.0413 (M^+; calcd for $C_{17}H_{14}DBr$, 299.0420).

Reaction of Bromide 15-*d* with *n*-Butyllithium. A solution of 0.600 g (2.00 mmol) of **15**-*d* in 15 mL of dry THF under nitrogen was treated at room temperature with 0.60 mL (1.28 mmol, 0.64 equiv) of 2.14 M *n*-butyllithium in hexane. The red solution was allowed to stand 30 min, during which time the color dissipated to yellow. Quenching (saturated NH_4Cl) followed by an aqueous methylene chloride workup yielded 630 mg of a pale yellow oil on concentration. NMR analysis revealed the presence of starting material (0.359 g, 60%) and 9-*n*-butyl-10-propenyl-3-*d*-9,10-dihydroanthracene (**16**-*d*; 0.222 g, 40%). A portion of the mixture was purified by preparative TLC (200-μm micron silica gel) with *n*-hexane elution: R_f 0.40 (**16**-*d*), 0.19 (**15**-*d*). NMR analysis of recovered **16**-*d* showed that the diastereotopic excess of deuterium is unaltered during reaction. The ^1H NMR spectrum ($CDCl_3$, 360 MHz) of the product indicates that all deuterium is located in the terminal vinyl positions (see Results).

Reduction of 15 with Tri-*n*-butyltin Hydride. A mixture of 2.99 g (10 mmol) of **15**, 2.91 g (10 mmol) of tri-*n*-butyltin hydride, and 0.035 g (2 mol %) azobis(isobutyronitrile) (AIBN) was heated in 50 mL of benzene under nitrogen at 80 °C for 2 h. Concentration provided 5.84 g of a mixture of white solid and a pale yellow oil. trituration with cold ethanol and filtration gave a mixture of 1.10 g (2.6 mmol) of recovered **15** and 11-methyl-9,10-ethano-9,10-dihydroanthracene (**23**). The mother liquors were concentrated, and 4.30 g of the residue was chromatographed on 75 g silica. Elution with petroleum ether afforded 1.27 g of **23** (cuts 6–9), and later fractions (cuts 11–18) gave some more **15**, making the material balance nearly quantitative. Compound **23** (76% total yield) was identical in all respects with an authentic sample.[21] No ring-opened compounds were detected in the reaction products.

Registry No. **1**, 1521-59-1; **1**·K, 84332-54-7; **2**, 120-12-7; **3**, 84332-55-8; **3**·K, 84332-56-9; **4**, 5910-32-7; **5**, 58746-82-0; **6**, 71870-46-7; **15**, 42166-01-8; **15**-d_1, 84332-62-7; **16**, 84332-61-6; **16**-d_1, 84332-63-8; **17**, 84332-59-2; **19**, 7673-68-9; **20**-d_1, 35964-05-7; **21**, 84332-57-0; **22**, 84332-58-1; **23**, 32363-36-3; TASF, 59218-87-0; 9-propenyl-10-(trimethylsilyl)-9,10-dihydroanthracene, 84332-60-5.

(21) Panker, V. D.; Dirlam, J. P.; Eberson, L. *Acta Chem. Scand.* **1971**, *25*, 341.

Synthesis of (*Z*,*Z*)-11,13-Hexadecadienal, a Principal Component of Navel Orangeworm (*Pamyelois transitella*) Pheromone

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This report outlines a commercial synthetic process for (*Z*,*Z*)-11,13-hexadecadienal (navel orangeworm pheromone). The synthetic scheme which is employed introduces the stereochemically labile conjugated diene moiety at a late stage in the synthesis, thereby avoiding complications during the purification of intermediates. In addition, the aldehyde function is generated through a Grignard reaction sequence, obviating the generally accepted techniques which are usually unsuitable for commercial preparations. We have also observed the first reported selective inclusion by urea of a conjugated (*Z*,*Z*)-diene as a means of mild purification of labile dienic pheromone intermediates.

As the first pheromone discovered to contain a *Z*,*Z* conjugated diene moiety, the navel orangeworm pheromone presents some unique challenges from a synthetic standpoint. Sonnet and Heath[1] followed the straightforward synthetic approach of generating the conjugated diene system through dialkylborane reduction of the appropriate diyne obtained from Cadiot–Chodkiewicz[2] coupling of the proper acetylenes as outlined in Scheme I.

This synthesis suffers from two weaknesses. It utilizes chromium oxidation[3] to generate the aldehyde, and 2 equiv of expensive dicyclohexylborane are necessary to reduce the diyne to the (*Z*,*Z*)-diene.

Results and Discussion

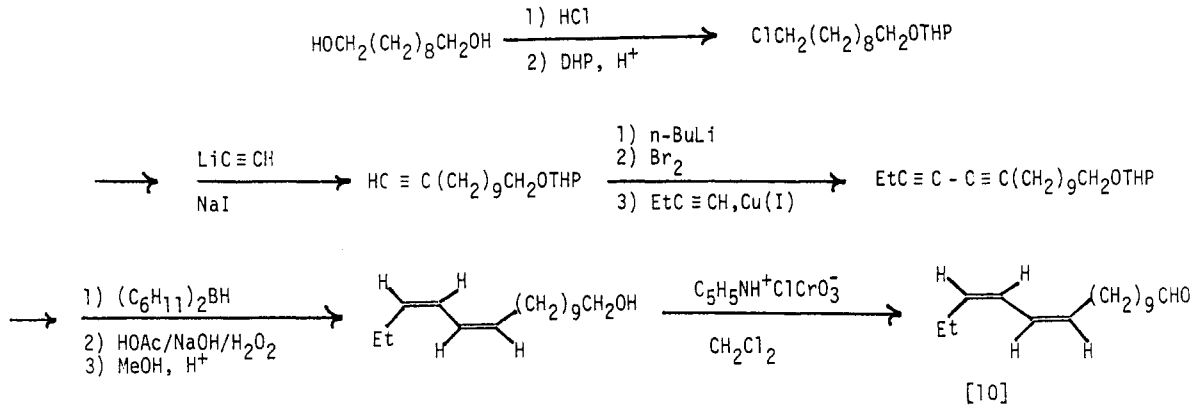
In our continuing search for a more convenient and cost-effective approach to the generation of the (*Z*,*Z*)-diene functionality, we found that dialkylborane reduction of the appropriate (*Z*)-enyne would afford the desired diene, thus requiring only half the expensive dialkylborane reagent

(1) Sonnet, P. E.; Heath, R. R. *J. Chem. Ecol.* **1980**, *6* (1), 221–8.
(2) Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, [13] 2, 819.

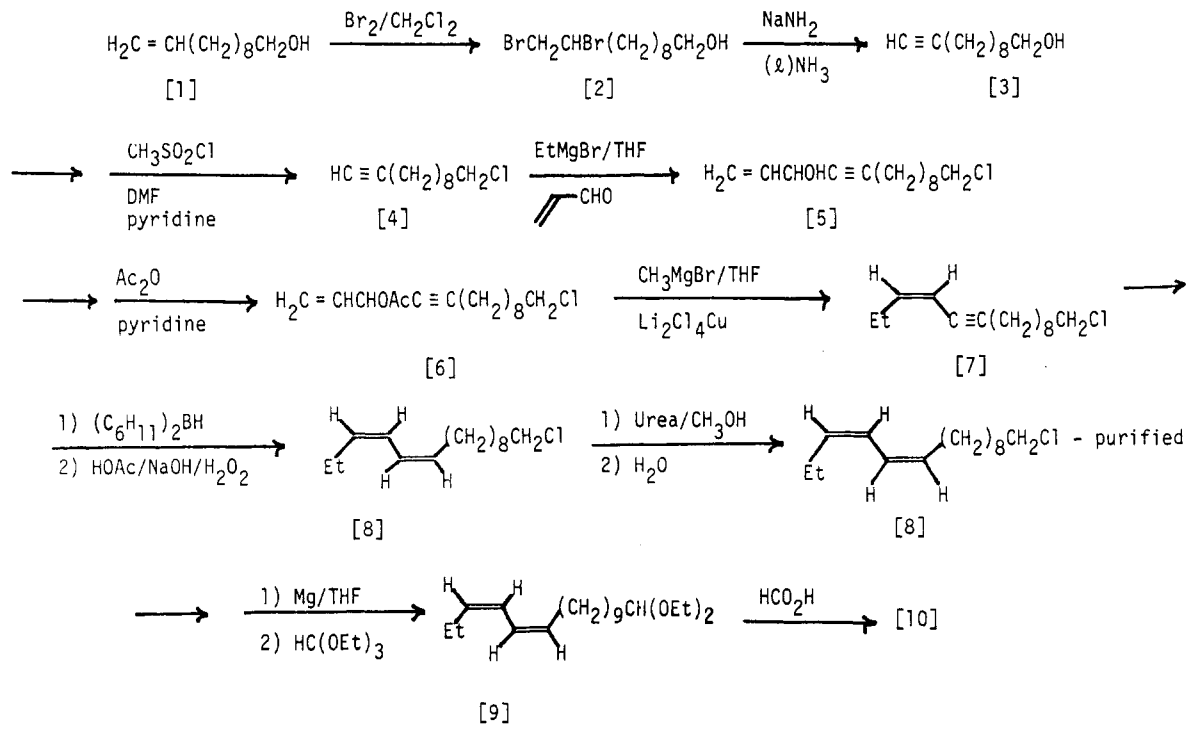
(3) In a commercial reaction sequence, chromium oxidations where possible are to be avoided due to the disposal problems that accompany such processes.

0022-3263/83/1948-0657$01.50/0

Scheme I



Scheme II



needed for the previous diyne system. With this approach, we have prepared (*Z*,*Z*)-11,13-hexadecadienal (**10**) as outlined in Scheme II.

The 10-undecyn-1-ol (**3**), obtained by bromination–dehydrobromination of undec-10-enyl alcohol (**1**), was treated with methanesulfonyl chloride/pyridine[4] in DMF to yield 11-chloro-1-undecyne[5] (**4**). Treatment of **4** with ethyl magnesium bromide in THF followed by condensation with acrolein yielded 14-chloro-1-tetradecen-4-yn-3-ol (**5**) which was treated with acetic anhydride/pyridine to yield the desired acetate (**6**). The conjugated (*Z*)-enyne moiety was obtained by treatment of **6** with methylmagnesium bromide in THF[6] and a catalytic amount of Li_2Cl_4Cu, yielding 15-chloro-(*Z*)-3-pentadecen-5-yne (**7**). This reaction proved to be highly stereospecific, producing enyne of nearly 99% *Z* configuration, with 15% of byproducts from side reactions and direct attack on the carbonyl function. Compound **7** also proved to be exceptionally stable and resistant to isomerization. Indeed, all attempts to isomerize the (*Z*)-enyne to an *E*/*Z* mixture with thiophenol/AIBN[7] or $NaNO_2/HNO_3$[8] proved fruitless. No thermal isomerization to the *E* isomer was observed when **7** was heated to 200 °C.

Following distillation, **7** was treated with dicyclohexylborane[9] to yield the desired 15-chloro-(*Z*,*Z*)-3,5-pentadecadiene (**8**).[10] Compound **8** was purified by urea inclusion,[11] converted to a Grignard reagent, and reacted

(4) Fujimoto, A.; Shimizu, T.; Tatsuno, T. *Chem. Pharm. Bull. Jpn.* **1976**, *24*, 356.

(5) This preparation provides an excellent example of the low reactivity of the chloro functionality as a blocking group in a synthetic sequence. The chloro substituent survived through five synthetic steps and was readily converted to the corresponding Grignard reagent to make the diethyl acetal. Utilization of a chloro blocking group avoids any chemical manipulation which could lead to isomerization of the sensitive diene functionality in later steps.

(6) Cassani, G.; Massadro, P.; Piccardi, P. *Tetrahedron Lett.* **1979**, 633–4.

(7) Bhalerao, V. T.; Rapoport, H. *J. Am. Chem. Soc.* **1971**, *93*, 4835. Amos, A.; Katzenellenbogen, J. A. *J. Org. Chem.* **1978**, *43*, 555–60.

(8) Sonnet, P. E. *J. Org. Chem.* **1974**, *39*, 3793.

(9) Zweifel, G.; Poston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068–7.

(10) During our investigation of this process, we had initially intended to convert 15-chloro-(*Z*)-3-pentadecen-5-yne (**7**) to a Grignard reagent, generate the acetal, and then reduce with a dialkylborane, thus placing a costly step closer to the end of the synthetic sequence at considerable savings. In our hands, this chloro enyne (**7**) proved to be inert toward magnesium even after entrainment techniques were employed. On the contrary, the chloro (*Z*,*Z*)-diene **8** converted readily to a Grignard reagent. This peculiar phenomenon may bear closer scrutiny.

with triethyl orthoformate to give (Z,Z)-11,13-hexadecadienal diethyl acetal (9).[12] Purification of this heat-sensitive compound[13] was effected by means of a thin-film evaporator whereby the distilled acetal was obtained with a minimum of isomerization of the diene functionality. Finally, cleavage of the acetal with formic acid yielded the desired (Z,Z)-11,13-hexadecadienal (10) as a clear, pale yellow liquid which was of sufficient purity and quality as to require no further purification. This synthetic approach proved to be attractive economically and quite amenable to large-scale production as we were able to prepare nearly 3 kg of (Z,Z)-11,13-hexadecadienal (10).

Experimental Section

Infrared spectra were recorded on a Beckmann Acculab 9 infrared spectrometer and standardized with polystyrene. A Bruker WM-300 spectrometer was used to obtain NMR spectra. The mass spectra were obtained with a Finnigan Model 4000 GC/MS spectrometer. All molecular mass ions were checked by electron impact and by chemical ionization. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

10,11-Dibromo-1-undecanol (2). Undec-10-enyl alcohol (1; 34 kg, 200 mol) was dissolved in 200 L of dichloromethane and cooled to −5 °C, and then 32 kg (200 mol) of liquid bromine was added over a 4-hr period, maintaining the temperature at 0 to −5 °C. After the addition, the reaction mixture was stirred an additional 4 h at 0 °C, and then the solvent was removed under vacuum (20 torr) to a pot temperature of 50 °C. The entire crude dibromide was used directly in the next step without further purification. The yield was quantitative.

10-Undecyn-1-ol (3). The crude dibromide from the preceding step was divided into 13 parts to facilitate handling in a 50-L ammonia reactor. A sample run follows. To 18 L of liquid ammonia was added 3.12 kg (65 mol) of sodium amide. After the mixture was stirred 15 min, 6.1 kg (18.5 mol) of the crude dibromide dissolved in 3.5 L of THF was added over a period of 1 h, stirred an additional 16 h, and then quenched with 2.27 kg of powdered ammonium chloride, followed by 24 L of water. Following layer separation, the organic layer (containing crude alcohol) was extracted four times with 0.5 volume of brine, and the aqueous layer was discarded. The organic layer was stabilized with a small amount of BHT (approximately 2 g) and subjected to short-path distillation at 120 °C (1 torr) to yield (after combining 13 runs as above) 26.17 kg (155.8 mol) of 10-undecyn-1-ol (3). The yield based on undecylenic alcohol was 78%. The product was identical with a known sample of 3 in all respects.

11-Chloro-1-undecyne (4). 10-Undecyn-1-ol (3; 26.17 kg, 155.8 mol) was added to a reactor along with 73.4 kg of DMF and 13.6 kg of pyridine. To this stirred mixture under nitrogen was added 19.55 kg (170 mol) of methanesulfonyl chloride over a period of 4 h, maintaining the temperature at 20–25 °C. The mixture was stirred an additional 1 h at 20–to 25 °C and then slowly heated to 75–85 °C and held there for 12 h. Following this period, the reaction mixture was sampled and extracted several times with water, and the organic layer was dried over sodium sulfate. GC analysis on a Carbowax 20M column showed no remaining alcohol or its corresponding mesylate to be present. A GC spike with authentic 11-chloro-1-undecyne showed this to be the only major product present. The reaction mixture was cooled to about 50 °C whereupon 50 gal of water was added along with 7 gal of hexane. After extraction, the lower aqueous phase was discarded, and the hexane/product layer was extracted twice with 15 gal of brine. After distilling the hexane solution at atmospheric pressure to dry the product, the product was isolated by short-path distillation at 100 °C (3 torr) and then redistilled on a metal-packed column of about 30 plates efficiency to yield 18 kg (96.5 mol) of 95% pure 11-chloro-1-undecyne (4): yield from the alcohol was 62%; bp 49–54 °C (0.1 torr); IR (neat) 3270 cm^{-1}; NMR ($CDCl_3$) δ 1.74 (m, 2, J = 6.5 Hz), 1.91 (t, 1, J = 2.54 Hz), 2.15 (dt, 2, J = 7.1 Hz), 3.5 (t, 2, J = 6.6 Hz), 1.2–1.6 (m, 12); mass spectrum, m/e 186 (M^+). Anal. Calcd for $C_{11}H_{19}Cl$: C, 70.75; H, 10.26; Cl, 18.99. Found: C, 71.00; H, 9.79; Cl, 18.97.

14-Chloro-1-tetradecen-4-yn-3-ol (5). The Grignard reaction was initiated with an aliquot of ethyl bromide added to magnesium turnings (2.58 kg, 106 mol) partially layered with THF under nitrogen. The exothermic reaction came to reflux, and the balance of ethyl bromide (11.55 kg, 106 mol, in 45 L of THF) was added over a 6-h period. The reaction mixture was allowed to stir an additional 2 h. Following this stir-out period, 11-chloro-1-undecyne (4, 18 kg, 96.5 mol) was added at reflux (~70 °C) over an 8-h period; the reaction mixture was allowed to stir at reflux for 9 h, after which time the reaction mixture was cooled to 25 °C. Next, a mixture of 5.3 kg (94.4 mol) of acrolein in 12 L of THF was added over a 2-h period, maintaining the temperature below 30 °C. After being stirred an additional 12 h, the reaction mixture was sampled, hydrolyzed with water, and analyzed by GC on a 6-ft Carbowax 20M column. Typical runs showed about 20% unreacted chloroundecyne 4 (recoverable), with the remainder being the desired alcohol 5. The reaction mixture was then cooled to 10 °C and hydrolyzed with a mixture of 9 L of water and 9 L of acetic acid. Hexane (9 L) was added, the reaction mixture was extracted, and the aqueous layer was discarded. The crude product in hexane was extracted three times with 0.5 volume brine and then distilled under vacuum to a pot temperature of 95 °C (2 torr). Crude alcohol 5 (13 kg) was isolated and used directly in the next step after the material was checked for dryness by Karl–Fischer titration (should be about 0.05% water or less before proceeding to the next step).

14-Chloro-1-tetradecen-4-yn-3-ol Acetate (6). To the crude alcohol 5 from the preceding step was added 2.34 kg (29.6 mol) of dry pyridine. Under nitrogen, 6 kg (59.2 mol) of acetic anhydride was added at room temperature over a 6-h period. After the mixture was stirred 2 h, a sample was analyzed by GC on a 6-ft Carbowax 20M column for the loss of alcohol 5 and the appearance of acetate 6. At completion of the reaction, the crude product was distilled to remove excess acetic anhydride and residual pyridine under a 2-torr vacuum. Finally, the product was distilled through a thin-film evaporator, the first pass to remove unreacted 11-chloro-1-undecyne (4) (3 torr, 100 °C) and the second pass to distill the product off the higher-boiling residues (3 torr, 170 °C). This yielded 15.3 kg (53.9 mol) of acetate 6 which was sufficiently pure to carry to the next step: yield 67% (based on 80% conversion of 11-chloro-1-undecyne (4)); IR (neat) 1734, 1355, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.2–1.6 (m, 13), 1.74 (m, 2, J = 7 Hz), 2.1 (s, 3), 2.23 (t, 2, J = 7 Hz), 3.5 (t, 2, J = 6.6 Hz), 5.2–6.0 (m, 3); mass spectrum, m/e 284 (M^+). Anal. Calcd for $C_{16}H_{25}O_2Cl$: C, 67.47; H, 8.85; Cl, 12.45; O, 11.23. Found: C, 67.28; H, 8.95; Cl, 12.50; O, 11.27.

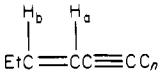
15-Chloro-(Z)-3-pentadecen-5-yne (7). A solution of 14-chloro-1-tetradecen-4-yn-3-ol acetate (6; 15.3 kg, 53.8 mol) in 17.5 L of THF was charged to a reaction vessel along with 17 L of standard Li_2Cl_4Cu solution (13.5 g of $CuCl_2$ and 8.5 g LiCl/1 L of THF as the standard solution) and cooled to −30 °C under nitrogen. To this stirred cool solution was added 57.9 mol of 1.5 M methylmagnesium bromide solution in THF over a 4-h period, maintaining the reaction pot temperature at −30 °C throughout. The reaction mixture was then allowed to warm to room temperature over 3 h. The reaction mixture was sampled and hydrolyzed with acetic acid/water and checked by GC on a Carbowax 20M column. Analysis revealed the absence of the starting acetate 6 and the presence of a cluster of one major and three minor peaks, the major peak being the desired 15-chloro-(Z)-3-pentadecen-5-yne (7). Holding the reaction mixture below 25 °C, a solution of 5 L of acetic acid in 6 L of water was added with stirring, after which the layers were separated, and the organic layer was extracted twice with 0.5 volume of saturated brine. After vacuum distillation of residual THF, the product was isolated by short-path distillation at 130 °C (1 torr). The crude product was then distilled on a 2

(11) Leadbetter, G.; Plimmer, J. R. *J. Chem. Ecol.* **1979**, *5* (1) 101–8. Noteworthy is the fact that no previous information on the formation of urea inclusion complexes with conjugated (Z,Z)-dienes has been reported. The use of the chloride facilitated this complex formation. An effective purification was shown not to be possible at the bulky acetal (9) stage.

(12) Stetter, J.; Reske, E. *Chem. Ber.* **1970**, *103*, 643–4. We have observed significant yield increases in the laboratory by the use of diethyl phenyl orthoformate in place in triethyl orthoformate in the preparation of the acetal 9.

(13) During purification there is some conversion of acetal to vinyl ethers, which likewise convert to aldehydes upon treatment with formic acid.

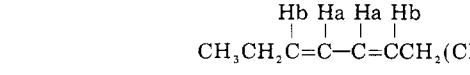
in. × 4 ft metal packed column to yield 5.8 kg (24.1 mol) of 99% 15-chloro-(*Z*)-3-pentadecen-5-yne (**7**), bp 77–86 °C (0.3 torr). The product contained less than 1% of the *E* isomer as determined by GC on a 20-m CC-52 glass capillary column operated isothermally at 195 °C. The yield of **7** from the starting acetate **6** was 45%: IR (neat) 1625 cm^{-1} (weak); NMR ($CDCl_3$) δ 1.03 (t, 3, J = 7 Hz), 1.30–1.48 (m, 12), 1.54 (m, 2, J = 7 Hz), 1.76 (m, 2, J = 6.7 Hz), 2.3 (m, 2), 3.52 (t, 2, J = 6.7 Hz), 5.4 (d, Ha, 1,



J = 11 Hz), 5.8 (dt, Hb, 1, J = 11, 7.26 Hz); mass spectrum, m/e 240 (M^+). Anal. Calcd for $C_{15}H_{25}Cl$: C, 74.81; H, 10.47; Cl, 14.72. Found: C, 74.70; H, 10.26; Cl, 14.63.

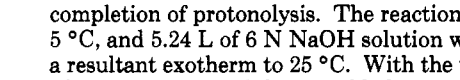
15-Chloro-(*Z*,*Z*)-3,5-pentadecadiene (8). The 5.8 kg (24.1 mol) of enyne chloride **7** was divided into four equal parts to facilitate handling. A typical run was as follows. To 7 L of a 1.0 M BH_3·THF complex solution was added 1.26 kg (15.4 mol) of cyclohexene at 2–10 °C over a 2-h period after which the resulting dicyclohexylborane suspension was allowed to stir an additional 4 h at 5–10 °C. In another reaction vessel was placed 1.5 kg (6.24 mol) of 15-chloro-(*Z*)-3-pentadecen-5-yne (**7**) in 1.75 L of dry THF and the mixture cooled to −10 °C under nitrogen. The previously prepared dicyclohexylborane/THF suspension was added to the enzyne/THF solution at −10 °C over a 2-h period after which the reaction mixture was allowed to warm to room temperature and stirred an additional 12 h. Following reaction completion the workup was as follows. Acetic acid (1.57 L) was added to the reaction mixture over a 1-h period at 30 °C, and the temperature was raised to 55 °C and maintained for an additional 5 h to ensure completion of protonolysis. The reaction mixture was cooled to 5 °C, and 5.24 L of 6 N NaOH solution was added quickly with a resultant exotherm to 25 °C. With the temperature held at 30 °C, 1.04 L of 47% H_2O_2 was added over a 2-h period followed by 15 min of additional stirring. Hexane (1 gal) was added to assist in layer separation. The lower aqueous phase was discarded and the product/THF/hexane layer was extracted five times with 0.5 volume of saturated brine, followed by vacuum distillation of the solvents, keeping the pot temperature below 50 °C. The crude 15-chloro-(*Z*,*Z*)-3,5-pentadecadiene (**8**) thus obtained was ready for purification by urea inclusion.

Isolation of Pure 15-Chloro-(*Z*,*Z*)-3,5-pentadecadiene (8). The crude product **8** from the preceding preparation was divided into several parts and treated as follows. To 9 L of methanol was added 4.45 kg of urea, and the resulting slurry was stirred and heated to 60 °C. Following the dissolution of urea, 1.28 kg of crude chloro diene **8** (contains approximately 500 g of cyclohexanol) was added quickly, whereupon, a fine, white precipitate immediately began to separate. This slurry was stirred, allowed to cool at its own rate to room temperature, and then filtered through a Büchner funnel. The filter cake was washed twice with 1 L of hexane, suctioned to dryness, and then added to 12 L of hot water with stirring. After addition of 1 L of hexane to the stirred mixture, the layers were allowed to separate, and the aqueous phase was discarded. The organic layer was extracted twice with 0.5 volume of saturated brine and then vacuum distilled at 1 torr to 50 °C. In this way, after combination of several runs, 15-chloro-(*Z*,*Z*)-3,5-pentadecadiene (**8**) was obtained: 4.6 kg (19 mol); yield 79% (overall from enyne **7**); IR (neat) 1645, 1590 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 3, J = 7.4 Hz), 1.29–1.40 (m, 12), 1.75 (m, 2, J = 7 Hz), 2.17 (m, 4), 3.53 (t, 2, J = 6.8 Hz), 5.44 [dt, 2, Hb, J



= 7.2 Hz; on irradiation at δ 2.28, Hb collapsed to a doublet J(cis) = 9.5 Hz], 6.23 (m, 2, Ha); mass spectrum, m/e 242 (M^+). Anal. Calcd for $C_{15}H_{27}Cl$: C, 74.19; H, 11.21; Cl, 14.60. Found: C, 74.26; H, 11.26; Cl, 14.54.

(*Z*,*Z*)-11,13-Hexadecadienal Diethyl Acetal (9). The Grignard reagent of chloro diene **8** (4.6 kg, 19 mol) was prepared in the usual fashion in THF at reflux temperature to a strength of 2.0 M. Next, 2.8 kg (19 mol) of triethyl orthoformate was added slowly with removal (by means of a distillation head) of enough THF to raise the pot temperature to 95 °C. Following the addition of triethyl orthoformate, the reaction was stirred at 95 °C for 48 h. The reaction was deemed complete when the ratio of product to (*Z*,*Z*)-3,5-pentadecadiene (product of hydrolysis of the Grignard reagent) was about 7.5:1. The reaction mixture was then cooled to 30 °C and hydrolyzed with 1.7 L of water, and the organic layer was decanted from the resulting magnesium salts which were subsequently washed with 1 L of THF. The combined organic layers were washed three times with 0.5 volume of saturated brine and once with 0.5 volume of dilute sodium carbonate solution until basic. The organics were then vacuum distilled to a pot temperature of 50 °C at 1 torr. The resulting crude acetal was now ready for distillation through a 2-in. Pope thin-film evaporator. The first pass at 135–140 °C (0.5 torr) removed the hydrocarbon byproduct [(*Z*,*Z*)-3,5-pentadecadiene] containing about 20% acetal in the distillate. The resulting crude acetal contained less than 2% hydrocarbon impurity and was passed through the evaporator again to distill the product acetal **9** at 175–180 °C (0.5 torr). The resulting thick residue was found to contain less than 2% acetal after pass two and was discarded. The distillate from pass one was redistilled through the evaporator at 150 °C (0.5 torr) to concentrate the contained acetal **9** which, following this pass, contained less than 2% hydrocarbon impurity. In this manner, 3.8 kg (12.26 mol) of (*Z*,*Z*)-3,13-hexadecadienal diethyl acetal (**9**) was obtained at an overall purity of 95.7% (excluding isomeric impurities), containing 1.27% of (*Z*,*Z*)-3,5-pentadecadiene and 2.35% of an impurity believed to be a monoolefinic acetal. The distilled product acetal **9** was carried to the next step without further treatment: yield 65% (based on the chloro diene **8**); IR (neat) 1645, 1590, 1130, 1050 cm^{-1}; NMR ($CDCl_3$) δ 0.97 (t, 3, J = 7.5 Hz), 1.18 (t, 6, J = 7.1 Hz), 1.25–1.48 (m, 14), 1.58 (dt, 2), 2.15 (m, 4), 3.55 (m, 4), 4.45 (t, 1, J = 5.8 Hz), 5.44 [m, 2, Hb, Hb



collapsed to a doublet after irradiation at δ 2.28 to give J(cis) = 9.1 Hz], 6.23 (m, 2, Ha); mass spectrum, m/e 310 (M^+). Anal. Calcd for $C_{20}H_{38}O_2$: C, 77.36; H, 12.34; O, 10.30. Found: C, 77.18; H, 12.23; O, 10.59.

(*Z*,*Z*)-11,13-Hexadecadienal (10). The distilled acetal **9** (3.8 kg, 12.26 mol) was placed in a reaction flask along with 36.8 mol (1.7 kg) of 90% formic acid and heated with vigorous stirring to a pot temperature of 75 °C until a reflux of ethyl formate ensued. By means of a distillation head, the ethyl formate was removed until the pot temperature rose to 95 °C. At this point, the ethyl formate had ceased to distill, and the reaction mixture was cooled to 35 °C under nitrogen. Residual excess formic acid was separated and discarded. The neat aldehyde was extracted three times with 0.5 volume of saturated brine. Finally, the product was placed in a stirred, heated flask, and vacuum was applied to remove residual water and ethyl formate to a pot temperature of 50 °C at 1 torr. The resulting aldehyde product was filtered through a glass wool plug and stored in aluminum bottles. Analysis of a sample on a 20-m CC-52 glass capillary column at 195 °C gave the following results: (*Z*,*Z*)-11,13-hexadecadienal (**10**), 90.0%) with 3.53% *Z*,*E* isomer (plus 1.27% hydrocarbon and 2.35% monoolefinics). Thus, 2.8 kg of (*Z*,*Z*)-11,13-hexadecadienal was obtained at a yield of 97% from the acetal **9**: IR (neat) 1715, 1645, 1590 cm^{-1}; NMR ($CDCl_3$) δ 1.01 (t, 3, J = 7.4 Hz), 1.20–1.39 (m, 12), 1.60 (m, 2), 2.18 (m, 4), 2.40 (dt, 2, J = 7.4, 1.7 Hz), 5.43 [m, 2; irradiation at δ 2.28 reduced this to a doublet, J(cis) = 9.7 Hz], 6.23 (m, 2), 9.75 (t, 1, J = 1.7 Hz); mass spectrum, m/e 236 (M^+). Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94; O, 6.77. Found: C, 81.77; H, 11.82; O, 7.01.

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Registry No. **1**, 112-43-6; **2**, 24724-18-3; **3**, 2774-84-7; **4**, 29043-93-4; **5**, 84433-04-5; **6**, 84433-05-6; **7**, 84433-06-7; **8**, 71317-67-4; **9**, 71673-23-9; **10**, 71317-73-2; $HC(OEt)_3$, 122-51-0; acrolein, 107-02-8; urea, 57-13-6; diethyl phenyl orthoformate, 14444-77-0.