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Preparation of (*E*)-1,3,5-Hexatriene and (3*E*, 5*E*)-1,3,5,7-Octatetraene by the Palladium Catalyzed Elimination of Acetic Acid from Allylic Acetates

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Synopsis. Palladium complex-catalyzed elimination of acetic acid from (2*E*,4*E*)-2,4-hexadienyl acetate and (2*E*, 4*E*, 6*E*)-2,4,6-octatrienyl acetate afforded, respectively, the title conjugated polyenes stereoselectively.

Recently, a simple preparative method for terminal conjugated dienes by palladium complex-catalyzed elimination of acetic acid and phenol from easily available allylic acetates and phenyl ethers, has been developed in this laboratory[1] and by Trost *et al.*[2]

The elimination reaction can be explained *via* the formation of a π-allylic palladium complex by oxidative addition of allylic compounds to Pd(0) species. Elimination of acetic acid or phenol is nonstereoselective insofar as each hydrogen α to the π-allylic system in the complex is eliminated, resulting in the formation of a mixture of (*E*)- and (*Z*)-isomers for simple 1,3-dienes.

This method may be of synthetic value for conjugated polyenes as well, especially if stereochemical limitation can be obviated. We wish to present a stereoselective preparation of (*E*)-1,3,5-hexatriene and (3*E*,5*E*)-1,3,5,7-octatetraene by way of the palladium complex-catalyzed elimination. Pyrolytic routes to these polyenes hitherto reported are usually nonstereoselective.

(2*E*,4*E*)-2,4-Hexadienyl acetate (**1**), derived from commercial (2*E*,4*E*)-2,4-hexadien-1-ol (isomeric purity >98%), was heated at reflux in toluene with palladium(II) acetate (1.0 mol%) and excess triphenylphosphine. 1,3,5-Hexatriene[3,4] was obtained by fractional distillation in 87% yield prior to the distillation of acetic acid eliminated. GLC analysis showed the triene to consist of (*E*)- and (*Z*)-isomers at least in a ratio of 97 : 3. IR spectrum of the product indicated characteristic bands of the (*E*)-isomer.

The Diels-Alder adduct of (*E*)-1,3,5-hexatriene with maleic anhydride was prepared for further structural characterization. ^{13}C NMR data for the adduct, 3-vinyl-1,2,3,6-tetrahydrophthalic anhydride[4] (Table 1) indicate high diastereomeric purity which should arise from (*E*)-triene.

On the other hand, the same procedure as above with use of 1-vinyl-3-butenyl acetate (**2**) afforded the triene in 67% yield. GLC analysis revealed isomeric hexatrienes in the ratio 80 : 20. The (*E*)-isomer as a major component was confirmed by IR spectrum. Nonstereoselective elimination of acetic acid from **2** was found to take place. ^{13}C NMR data of the Diels-Alder adduct obtained with this sample are also given in Table 1. Three pairs of signals, which are unambiguously assigned to C_4, C_5, and C_8, respectively, stem from the adduct of the (*Z*)-triene in addition to that of the (*E*)-isomer.

It is noteworthy that the formal 1,ω-elimination of acetic acid from **1** took place as readily as 1,2-elimination to give (*E*)-hexatriene stereoselectively, whereas the 1,2-elimination from **2** gave an *E*/*Z* mixture. The results are related to the fact that the intermediate π-allylic palladium(II) complexes are apt to take *syn* configuration.

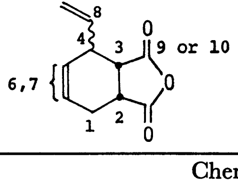
As an extension, (2*E*,4*E*,6*E*)-2,4,6-octatrienyl acetate (**3**) was prepared by the Wittig reaction of (ethoxycarbonylmethylene)triphenylphosphorane with (2*E*,4*E*)-2,4-hexadienal followed by lithium aluminium hydride reduction and acetylation. The trienyl acetate **3** was subjected to palladium complex-catalyzed elimination of acetic acid to give white, waxy crystalline (3*E*,5*E*)-1,3,5,7-octatetraene[5] in 48% yield. IR spectrum of the product indicated the *trans* structure.

Experimental

Materials. (2*E*, 4*E*)-2,4-Hexadienyl acetate (**1**)[6] was prepared by acetylation of commercial (2*E*, 4*E*)-2,4-hexadien-1-ol (6.00 g, 60 mmol) with acetic anhydride (11.4 mL, 120 mmol) and excess pyridine in 82% yield, bp 83—84 °C/19 Torr (1 Torr=133.322 Pa). GLC (PEG 20 M 3 m, at 160 °C) analysis indicated the isomeric purity to be >98%.

1-Vinyl-3-butenyl acetate (**2**) was prepared by the method

TABLE 1. ^{13}C NMR DATA FOR 3-VINYL-1,2,3,6-TETRAHYDROPHTHALIC ANHYDRIDE



1,3,5-Hexatriene	Chemical shifts, δ/ppm									
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
E(Pure)	22.8_4	38.8_4	39.5_1	45.1_8	118.4_8	127.3_4	130.3_4	134.5_0	171.4_3	174.1_3
E/*Z*(Mixture)	22.9_0	38.8_1	39.5_7	45.2_1	118.4_8	127.3_4	130.3_4	134.6_2	171.5_5	174.1_9
				44.5_0	115.7_8			135.8_6		

reported,[3] bp 56—57 °C/18 Torr.

*(2*E*, 4*E*, 6*E*)-2,4,6-Octatrienyl Acetate (3).* (i) A mixture of (ethoxycarbonylmethylene)triphenylphosphorane (2.93 g, 8.4 mmol) and freshly distilled (2*E*, 4*E*)-2,4-hexadienal (0.81 g, 8.4 mmol) dissolved in dry benzene (20 mL) was heated under argon atmosphere at 60 °C for 3.5 h. Evaporation of the reaction mixture and trituration of the residue with ether follwed by filtration were repeated three times to give phosphine oxide in 98% combined yield. The final filtrate was evaporated to dryness to give crude waxy ethyl (2*E*, 4*E*, 6*E*)-2,4,6-octatrienoate,[7] 1.30 g (93%). (ii) Lithium aluminium hydride reduction of the ester (1.22 g, 7.3 mmol) and acetylation of the resulting crude 2,4,6-octatrien-1-ol[5c] by the conventional procedure yielded **3**, 0.75 g (67%): bp 86—87 °C/3 Torr; ^{1}H NMR (CCl_4) δ 1.76 (t, J=5.6 Hz, MeCH=), 1.96 (s, MeCO), 4.45 (d, J=5.8 Hz, CH_2O), and 5.4—6.3 (m, olefinic protons); IR (neat) 1740 and 1240 cm^{-1}. GLC (PEG 20 M 3 m, at 180 °C) analysis of **3** appeared to cause significant decomposition.

Palladium Complex-catalyzed Elimination from Allylic Acetates. A typical procedure is as follows. A mixture of **1** (5.61 g, 40 mmol), palladium(II) acetate (91 mg, 0.4 mmol), and triphenylphsophine (1.05 g, 4.0 mmol) dissolved in dry toluene (30 mL) was heated at reflux under argon atmosphere. Low-boiling substances formed soon were fractionated through a column packed with glass helices (8×200 mm) until an azeotropic mixture of acetic acid with toluene was distilled. The distillate (bp 78—90 °C) was fractionated again to give a colorless oil, bp 80—83 °C (lit,[3] bp 80.5 °C), 2.42 g (95% purity by NMR, 87% yield) contaminated with a small amount of toluene and acetic acid. GLC (UCON 3 m, at 45 °C) analysis of the triene indicated that a principal peak is accompanied by a small peak, with a little longer retention time, in a ratio of 97 : 3. IR (neat): Characteristic bands of (*E*)-1,3,5-hexatriene are at 1430, 1010, and 940 cm^{-1}; lit,[8] 1429, 1011, and 941 cm^{-1}.

Similarly, 1,3,5-hexatriene was obtained by use of **2** (4.20 g, 30 mmol), bp 78—83 °C, 1.60 g (67%). GLC analysis of the product indicated that the isomeric composition is 4 : 1: IR (neat) 1430, 1010, and 940 cm^{-1} for the (*E*)-isomer, and 1450, 985, and 820 cm^{-1} for the (*Z*)-isomer; lit,[8] 1451, 987, and 818 cm^{-1}.

The acetate **3** (1.05 g, 6.3 mmol) was similarly heated in diethylene glycol diethyl ether (8 mL) in the presence of palladium(II) acetate (1 mol%) with added triphenylphosphine. Fractional distillation under reduced pressure (113 Torr) gave white, way crystalline (3*E*, 5*E*)-1,3,5,7-octatetraene, 0.33 g (48%), bp 89—93 °C/113 Torr, mp 50 °C; ^{1}H NMR (CCl_4) δ 4.90—5.30 (m, 4H) and 6.13 (br s, 6H); IR (CCl_4) 1010 and 900 cm^{-1} for the (*E*, *E*)-configuration.[5b] Octatetraene is rather unstable in the air, giving an insoluble polymeric material.

Diels-Alder Reaction. A mixture of (*E*)-1,3,5-hexatriene (1.40 g, crude fraction, 85% purity) and excess maleic anhydride (3.92 g, 40 mmol) in dioxane (10 mL) was stirred at room temperature for 3 d. After removal of the solvent under reduced pressure, the residue was chromatographed (silica gel, hexane–ethyl acetate, 10 : 1) to give 3-vinyl-1,2,3,6-tetrahydrophthalic anhydride[4] (1.18 g, 40%).

In the case of an isomeric mixture of (*E*)- and (*Z*)-hexatriene obtained by the elimination of **2** (1.12 g, 8.0 mmol), the crude fraction was heated at 60 °C for 2 d with maleic anhydride (2.94 g, 30 mmol) in dioxane under argon. Chromatographic purification as above gave the adduct (0.54 g, 38%).

^{13}C NMR ($CDCl_3$) data for the purified adducts are given in Table 1. Diels-Alder reaction of the tetraene with excess maleic anhydride in toluene at 60 °C under argon afforded a white powder after chromatographic purification in low yield, mp 136—139 °C (lit,[5a] 238—242 °C). No useful assignment of ^{13}C NMR data for the adduct could be made.

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