

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

Keiji YAMAMOTO,* Shigeaki SUZUKI, and Jiro TSUJI

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

(Received January 30, 1981)

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 laboratory¹ 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. ¹³C NMR data for the adduct, 3-vinyl-1,2,3,6-tetrahydrophthalic anhydride⁴) (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. ¹³C 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 C₄, C₅, and C₈, 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.

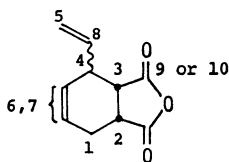
As an extension, (2*E*,4*E*,6*E*)-2,4,6-octatrienyl acetate (**3**) was prepared by the Wittig reaction of (ethoxycarbonylmethylene)triphenylphosphorane with (2*E*,4*E*)-2,4-hexadienal followed by lithium aluminium hydride reduction and acetylation. The trienyl acetate **3** was subjected to palladium complex-catalyzed elimination of acetic acid to give white, waxy crystalline (3*E*,5*E*)-1,3,5,7-octatetraene⁵) 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. ¹³C 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
<i>E</i> (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
<i>E/Z</i> (Mixture)	22.9 ₀	38.8 ₁	39.5 ₇	45.2 ₁ 44.5 ₀	118.4 ₈ 115.7 ₈	127.3 ₄	130.3 ₄	134.6 ₂ 135.8 ₆	171.5 ₅	174.1 ₉

reported,³⁾ bp 56–57 °C/18 Torr.

(2E, 4E, 6E)-2,4,6-Octatrienyl Acetate (**3**). (i) A mixture of (ethoxycarbonylmethylene)triphenylphosphorane (2.93 g, 8.4 mmol) and freshly distilled (2E, 4E)-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 followed 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 (2E, 4E, 6E)-2,4,6-octatrienoate,⁷⁾ 1.30 g (93%). (ii) Lithium aluminum hydride reduction of the ester (1.22 g, 7.3 mmol) and acetylation of the resulting crude 2,4,6-octatrien-1-ol^{6c)} by the conventional procedure yielded **3**, 0.75 g (67%): bp 86–87 °C/3 Torr; ¹H NMR (CCl₄) δ 1.76 (t, *J* = 5.6 Hz, MeCH=), 1.96 (s, MeCO), 4.45 (d, *J* = 5.8 Hz, CH₂O), 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 triphenylphosphine (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, waxy crystalline (3E, 5E)-1,3,5,7-octatetraene, 0.33 g (48%), bp 89–93 °C/113 Torr, mp 50 °C; ¹H NMR (CCl₄) δ 4.90–5.30 (m, 4H) and 6.13 (br s, 6H); IR (CCl₄) 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 anhydride⁴⁾ (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%).

¹³C NMR (CDCl₃) 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 ¹³C NMR data for the adduct could be made.

The authors thank Mr. Y. Nakamura for ¹³C NMR measurements and Mr. Y. Kimura for assisting in the experimental work.

References

- 1) a) J. Tsuji, T. Yamakawa, M. Kaito, and T. Mandai, *Tetrahedron Lett.*, **1978**, 2075; b) T. Mandai, H. Yasuda, M. Kaito, and J. Tsuji, and R. Yamaoka, and H. Fukami, *Tetrahedron*, **35**, 309 (1979).
- 2) B. M. Trost, T. R. Verhoeven, and J. M. Fortunak, *Tetrahedron Lett.*, **1979**, 2301. For related work, see: R. O. Hutchins, K. Learn, and R. P. Fulton, *ibid.*, **21**, 27 (1980).
- 3) J. C. H. Hwa and H. Sims, *Org. Synth.*, Coll. Vol. 5, 608 (1973).
- 4) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **70**, 3394 (1948); M. S. Schneider and M. Schnaithmann, *ibid.*, **101**, 254 (1979).
- 5) a) G. F. Woods and L. H. Schwartzman, *J. Am. Chem. Soc.*, **71**, 1396 (1949); b) E. R. Lippincott, W. R. Fairfeller, Jr., and C. E. White, *ibid.*, **81**, 1316 (1959); c) D. F. Evans, *J. Chem. Soc.*, **1961**, 2566.
- 6) P. Maginiac, *Ann. Chim. (Paris)*, **7**, 445 (1962).
- 7) V. F. Kucherov, B. G. Kovalev, I. I. Nazarova, and L. A. Yanovskaya, *Izv. Akad. Nauk SSSR, Otdl. Khim. Nauk*, **1960**, 1512 [*Chem. Abstr.*, **55**, 1420d (1961)].
- 8) J. C. H. Hwa, P. L. DeBenneville, and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).