organic extracts were washed with two 50-mL portions of 1 N potassium bicarbonate and a 50-mL portion of saturated aqueous sodium chloride. The organic solution was dried over potassium carbonate, and evaporation of the solvent at reduced pressure yielded 2.0 g of material. The ^{13}C NMR spectrum showed peaks for both C=O (216 ppm) and C—OH (79 ppm), and this indicated only partial conversion to **2a**.

The reaction with *tert*-butyllithium was therefore repeated four additional times at which point no further decrease was observed in the intensity of the ^{13}C peak for the carbonyl group of 1. GLC analysis (10% Carbowax 20M, 175 °C, flow rate = 30 mL/min) suggested that unreacted starting material (1) and product (2) were present in a 30:70 ratio (with retention times of 7 and 9 min, respectively).

1-*tert*-Butyl-2-adamantanone. The crude alcohol (ca. 3 g) was dissolved in 75 mL of reagent grade acetone in a 300-mL flask, and 5 mL (40 mequiv) of Jones reagent[13] was added dropwise over 10 min with magnetic stirring. The reaction mixture was stirred at room temperature for 12 h, and the excess oxident was destroyed by adding 2-propanol until the red color had disappeared. The reaction mixture was poured onto 200 g of ice, and the aqueous mixture was extracted with three 50-mL portions of chloroform. The combined chloroform extracts were washed with two 50-mL portions of 1 N potassium bicarbonate and a single portion of saturated aqueous sodium chloride and were dried over sodium sulfate.

The solvent was evaporated at reduced pressure, and the residue was purified by chromatography on alumina. Elution with petroleum ether (bp 30–60 °C) afforded 0.27 g of 1-*tert*-butyl-2-adamantanone (**4a**) as a colorless solid (crude mp 114–115 °C), followed by fractions which appeared to be a mixture of the desired product and unreacted protoadamantanone (1). Subsequent elution with diethyl ether yielded material that was identified as 1-adamantanol on the basis of spectroscopic properties and GLC behavior. Kugelrohr distillation of **4a** (0.1 torr, 150 °C bath temperature) followed by several recrystallizations from petane provided material melting at 126–127 °C. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.69; H, 10.86.

The proton NMR spectrum of **4a** ($CDCl_3$, Me_4Si) exhibits a sharp singlet at 1.0 ppm (9 H, *t*-Bu), a broad singlet at 2.5 ppm (1 H, H_a), and complex absorption between 1.1 and 2.2 ppm (12 H). See Table I for a complete analysis. The infrared spectrum shows strong absorptions at 1710 (C=O) and 2870–3040 cm^{-1} (CH). The ^{13}C NMR spectrum exhibits nine resonances in accord with the proposed structure ($CDCl_3$, Me_4Si): 215 (C=O), 54.0, 48.9, 39.3, 38.8, 36.1, 34.4, 28.2, 25.4 ppm.

Lanthanide induced shifts of 4a were obtained with Eu(fod)$_3$[12] in CCl_4 solution, and spectra were recorded with an EM-360 spectrometer. The incremental dilution method[6,14] was employed. Unique bound shifts were measured for each of the nine types of hydrogen in the molecule. LIS were independently predicted for the proposed structure with the pseudocontact equation[15,16] by using k = 976.6 and a carbon–europium bond length of 2.5 Å as described previously.[6,7] The optimum agreement between experiment and prediction was observed for a carbon–oxygen–europium bond angle of 152° with a scaling factor[7] of 0.94. The scaled experimental shifts are summarized in Table I together with the predicted values for each type of hydrogen.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1, 27567-85-7; **2a**, 84580-03-0; **4a**, 84499-71-8; *tert*-butyllithium, 594-19-4.

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Anti Stereoselectivity in the Palladium(0)-Catalyzed Conversion of Propargylic Esters into Allenes by Phenylzinc Chloride

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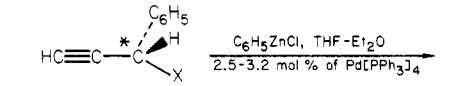
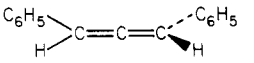
Recently we reported that the palladium(0)-catalyzed reaction of propargylic esters with organozinc compounds gives pure allenes.[1] The present paper concerns the stereochemistry of this synthetically useful reaction in both the steroid and the nonsteroid series.

In the nonsteroid series we studied the $Pd[PPh_3]_4$-promoted reaction of some esters derived from (*R*)-(–)-1-phenyl-2-propyn-1-ol with phenylzinc chloride and found that in all cases the induced 1,3-substitution proceeded with anti stereoselectivity to give the levorotatory allene (*R*)-**2**.[2]



(*R*)-**1a**, X = CH_3CO_2
b, X = CF_3CO_2
c, X = $CH_3S(O)O$



(1)

(*R*)-(–)-**2**

Comparison of the specific rotations, $[\alpha]^{20}_D$, measured for the produced allene **2** (see Experimental Section) with that reported for the optically pure allene, viz., –1137°,[3] showed that for all three conversions given in eq 1 the ratio of anti vs. syn 1,3-substitution was ca. 82/18. Apparently, the nature of the leaving group in ester **1** is not very important for the stereoselectivity of the reaction. From the literature it is known that phenylcopper also may be used to induce an anti 1,3-substitution in **1c**. The stereoselectivity in that case is better (ratio of anti vs. syn 1,3-substitution 88/12).[4]

In the steroid series three esters derived from mestranol (eq 2) were subjected to the reaction with phenylzinc chloride, again with $Pd[PPh_3]_4$ as the catalyst. In the steroid case the anti substitution product, compound **4**, can easily be distinguished from the epimeric syn substitution product, compound **5**, by ^1H NMR spectroscopy. The 13-Me signal for allene **4** is found as a sharp singlet at δ 1.07 and that for allene **5** at δ 0.95 (CCl_4, Me_4Si).[5] From the relative intensities of these peaks the product

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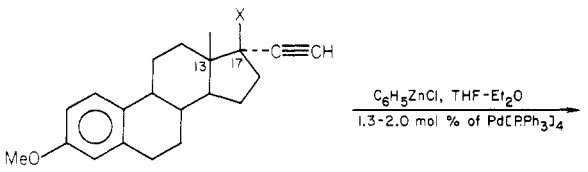
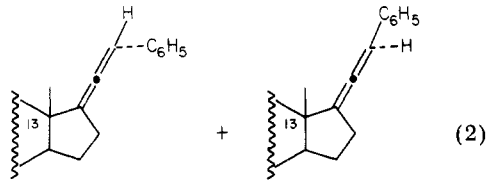


3a, X = CF_3CO_2
b, X = $CH_3S(O)O$
c, X = CH_3SO_3

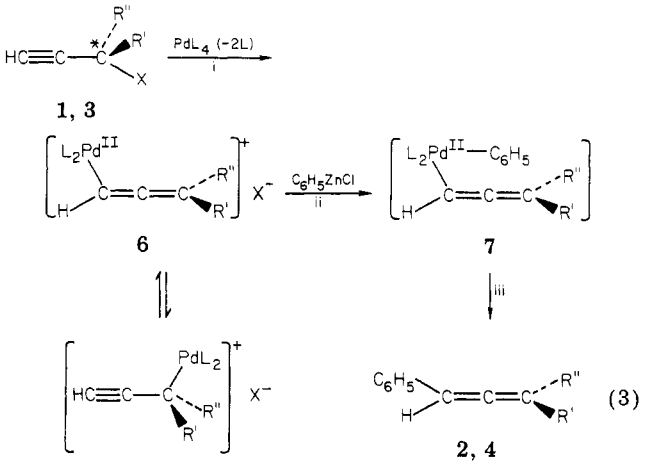


4 5 (2)

composition as obtained for the conversion of esters **3** by the phenylzinc reagent has been determined. The following ratios of **4**/**5** were found: 84/16 starting from **3a**, 98/2 starting from **3b**, and 88/12 starting from **3c**. These ratios were confirmed by optical rotation measurements (see the Experimental Section).

The product compositions show that the stereoselectivity of the reaction starting from **3a** and **3c** is comparable to the stereoselectivity found for the conversion of esters **1** into **2** (eq 1). Only the conversion of the sulfinate ester **3b** proceeds, by an hitherto unknown reason, with a much higher stereoselectivity. The stereoselectivity of this reaction is very close to that observed for the conversion of esters **3b** and **3c** by phenylcopper, reactions which proceed stereospecifically (cf. ref 5).

The origin of the anti substitution products is conceivable by assuming the following reaction sequence (eq 3):



L = PPh_3 (3)

(i) formation of the palladium(II) intermediate **6** from **1** or **3** with inversion, (ii) conversion of **6** into the palladium(II) intermediate **7** with retention, and (iii) reductive elimination of the end product from **7** with retention.

This route has also been proposed for palladium(0)-catalyzed reaction of allylic esters[6] and α-acetylenic epoxides[7] by organozinc compounds. The formation of the syn substitution products might be due to a partial loss of stereochemical integrity in one or more of the steps i–iii. The observation that in the steroid series the stereoselectivity depends on the nature of the leaving group X points in the direction that this loss of stereospecificity in the steroid case essentially occurs during step i. Formation of the syn substitution products by the direct displacement of the group PdL_2 from the palladium(II) compound **8**, the propargylic isomer of **6**, might also be possible if this displacement occurs with inversion. In fact, such a mechanism has been proposed to explain the palladium(0)-catalyzed formation of syn substitution products from allylic esters.[8]

Experimental Section

Materials. The acetate (*R*)-**1a** ($[\alpha]^{20}_D$ +0.1° (in EtOH); ee 28%)[9] and the trifluoroacetate (*R*)-**1b** ($[\alpha]^{20}_D$ −3.8° (in EtOH); ee 28%)[9] were obtained by reaction of 1.32 g of (*R*)-(−)-1-phenyl-2-propyn-1-ol (10 mmol; ee 28%) with butyllithium (10 mmol, 1.5 M solution in hexane) during 5 min at −60 °C (solvent: 30 mL of dry THF), followed by addition of 1.12 g of acetic anhydride (11 mmol) or 2.31 g of trifluoroacetic anhydride (11 mmol), stirring the mixture during 30 min at 25 °C, and isolation of the ester in the usual way. The sulfinate (*R*)-**1c** ($[\alpha]^{20}_D$ −16.7° (in EtOH); ee 27%)[9] was obtained from (*R*)-(−)-1-phenyl-2-propyn-1-ol (ee 27%) according to ref 10. The trifluoroacetate **3a** ($[\alpha]^{20}_D$ −11.5° (in CH_2Cl_2); ee 100%) was obtained by stirring 0.62 g of mestranol (2.0 mmol) in 20 mL of THF with 1.26 g of trifluoroacetic anhydride (6.0 mmol) and 0.60 g of triethylamine (6.0 mmol) during 40 min at 25 °C, followed by pouring of the mixture into 100 mL of water and isolation of the ester with hexane. The sulfinate **3b** ($[\alpha]^{20}_D$ −9.8° (in CH_2Cl_2); ee 100%) was prepared according to the procedure given in ref 10 and the sulfonate **3c** ($[\alpha]^{20}_D$ −2.6° (in CH_2Cl_2); ee 100%) according to the method described in ref 11. The catalyst $Pd[PPh_3]_4$ was obtained as indicated in ref 12 and was used as a 0.02 M solution in THF. $ZnCl_2$ was dried at 200 °C under high vacuum and was used as a 2.0 M solution in THF.

(a) Conversion of Esters 1a–c. To a stirred solution of 4.0 mmol of PhZnCl (prepared in situ by stirring 4.0 mmol of PhMgBr with 4.0 mmol of $ZnCl_2$ during 15 min at 25 °C with a mixture of 10 mL of dry THF and 7 mL of dry Et_2O as the solvent) were successively added, at −50 °C, 5 (esters **1a** and **1b**) or 6.4 mL (ester **1c**) of the $Pd[PPh_3]_4$ solution and 3.8 mmol of the ester **1**. The mixture was then allowed to warm to 25 °C in 15 min. In the case of ester **1a**, stirring at 25 °C was continued during 1 h; in the case of esters **1b** and **1c** the mixture was worked up without additional stirring. The allene was isolated by pouring the reaction mixture into 100 mL of an aqueous NH_4Cl solution, separating the organic layer, and extracting the water layer with pentane (2 × 50 mL). The combined organic layers were washed with water (5 × 50 mL) and dried (K_2CO_3); the solvent was evaporated under vacuum to give the allene in ca. 80% yield. The crude allene only contained some biphenyl (10–20 mol %) for which the specific rotation was corrected. The following $[\alpha]^{20}_D$ values were found (in EtOH): −203° starting from **1a**, −202° starting from **1b**, −197° starting from **1c**. Extrapolation to optically pure esters **1a–c** gives the following $[\alpha]^{20}_D$ values: −725°, −720°, and −730°, respectively.

(b) Conversion of Esters 3. To a stirred solution of PhZnCl (4.0 mmol in the case of ester **3a**, 6.0 mmol in the case of esters **3b** and **3c**) in a mixture of 10 mL of dry THF and 10 mL of dry Et_2O (see part a) were successively added, at −60 °C, 4 mL of the $Pd[PPh_3]_4$ solution and ester **3** (**3a**, 4.0 mmol; **3b** or **3c**, 3.0 mmol). The temperature of the resulting mixture was allowed to rise to 25 °C, and stirring was continued during 2 h at 25 °C. The mixture of allenes was isolated by pouring the reaction mixture into 100 mL of an aquous NH_4Cl solution and extracting with

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hexane (50 mL). The extract was washed with an aquous NH_4Cl solution (2 × 100 mL) and dried over $MgSO_4$. The solvent was evaporated in vacuum, and the crude mixture was analyzed by ^1H NMR spectroscopy in order to determine the ratio of **4**/**5**. These ratios were the following: 84/16 starting from **3a**, 98/2 starting from **3b**, and 88/12 starting from **3c**. Optical rotations were measured after purification of the crude allenes[13] by column chromatography (Al_2O_3 + 5% H_2O; eluent, hexane). The following specific rotations, $[\alpha]^{20}_D$, were measured (chemical yields of the allenes after purification are given in parentheses): -192° (51%) starting from **3a**, -270° (50%) starting from **3b**, -211° (80%) starting from **3c**.

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Registry No. **1a**, 84681-19-6; **1b**, 84681-20-9; **1c**, 70000-50-9; (*R*)-**2**, 49768-13-0; (*S*)-**2**, 3780-00-5; **3a**, 84681-21-0; **3b**, 36022-00-1; **3c**, 76685-96-6; **4**, 74055-34-8; **5**, 84693-98-1; (*R*)-1-phenyl-2-propyn-1-ol, 61317-73-5; mestranol, 72-33-3; PhZnCl, 28557-00-8; $Pd[PPh_3]_4$, 14221-01-3.

(13) The crude product contained ca. 10-20 mol % of mestranol from which the allene was purified by column chromatography.

Catalyzed Addition of Furan with Acrylic Monomers[1]

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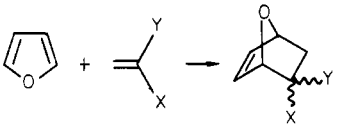
The 7-oxabicyclo[2.2.1]heptane system has been used in the synthesis of prostaglandins,[2] *C*-nucleosides,[3] muscarine analogues,[4,5] and antibiotics.[6] The most direct method to prepare these systems would be the Diels-Alder reaction of furan with various dienophiles. However, ring strain in the 7-oxabicyclo[2.2.1]heptane system and the aromatic character of the furan molecules combine to slow the rate of most of these reactions (Table I).

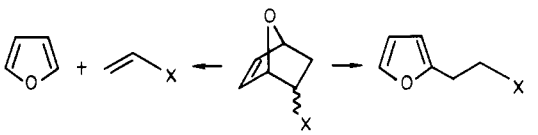
Strongly activated dienophiles such as acryloyl chloride and nitroethylene react readily with furan but are potent lachrymators and polymerize easily. The Diels-Alder reaction of furan and certain dienophiles may be accelerated by increasing the pressure on the reaction mixture. Dauben[11] has shown that at 15 000 atm, yields of about 50% are obtained after 4 h, and recently Kotsuki and Nishizawa[5] similarly prepared the adduct of furan and 2-chloroacrylonitrile. Unfortunately, 15 kbar equipment is not normally accessible for routine synthetic chemistry and is limited in reaction scale. Heating is often an ineffective expendient to increase the reaction rate, because the adducts of furan are thermally unstable and either decompose to furan and dienophile or are cleaved to a Michael-type product.

Table I. Some Diels-Alder Reactions with Furan



X	Y	time	yield, %
CO_2H	H	75 days	45[6]
		9 days	48[a]
CO_2Et	H	"several weeks"[b]	19[7]
CO_2Me	H	2-3 months	50[8]
		14 days	33[a]
CN	H	35 days	39[9]
		9 days	48[a]
CN	Cl	6 days	54
COCl	H	24 h	"high"[10]
NO_2	H	24 h	"high"[10]

[a] This work. Yields were determined by NMR. The reactions were conducted with a cupric fluoroborate concentration of 4.2 mol % and a hydroquinone concentration of 0.45 mol %, based on the concentration of dienophile. [b] Reaction temperature of 34 °C.



As part of our continuing interest in the synthesis of oxygenated bicyclic monomers[12] we sought to catalyze these reactions. Our attempts to use Lewis acids such as ferric chloride, stannic chloride, and zinc chloride with furan and different dienophiles yielded resinous products. Corey and co-workers[13] reported that cupric fluoroborate catalyzed the Diels-Alder reaction of cyclopentadiene derivatives and 2-chloroacrylonitrile. When we tried using cupric fluoroborate with furan and different, freshly distilled, acrylic monomers, no catalysis was observed. However, if hydroquinone (a polymerization inhibitor) was added, the rate of the Diels-Alder reaction[14] was greatly enhanced without changing the product stereochemistry. Thus, cupric fluoroborate alone does not catalyze the Diels-Alder reaction, but cupric fluoroborate and hydroquinone together catalyzed the reaction of furan with some acrylic monomers (Table I).

Dienophiles such as methacrylonitrile, methacrylic acid, methyl acrylate, vinylidene chloride, acrylamide, vinyl acetate, and styrene do not add to furan and could not be induced to react in the presence of copper(II)/hydroquinone either. A few dienophiles such as 2-chloroacrylic acid, maleic anhydride, and fumaronitrile react rapidly with furan, and the addition of copper(II)/hydroquinone causes no catalysis.

The reduction of Cu(II) to Cu(I) by hydroquinone was demonstrated spectroscopically by following the appearance of the characteristic quinone UV absorption at 243

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