ported by the National Science Foundation and the National Institutes of Health. We are grateful to R. L. Muntz for the initial preparation[16] of ketone **11**.

Registry No.—(±)-**1c**, 60686-64-8; (+)-**1c**, 60646-30-2; (−)-**1c**, 53531-34-3; **5a**, 19041-15-7; **5b**, 60686-65-9; **5c**, 60646-31-3; **5d**, 60646-32-4; **7**, 43119-29-5; **8**, 43119-28-4; **9**, 59829-44-6; **10**, 60646-33-5; **11**, 784-04-3; anthracene, 120-12-7; trifluoroacetic anhydride, 407-25-0; (4*S*,5*S*)-(−)-2-ethyl-4-hydroxymethyl-5-phenyl-2-oxazoline, 51594-33-3; ethyl levulinate, 539-88-8; diisopinocampheylborane, 1091-56-1; (*S*)-(+)-mandelic acid, 17199-29-0; chloromethyl methyl ether, 107-30-2; mandelic acid-d_1, 60646-34-6; 5-phenyl-1,3-dioxolan-4-one-5-*d*, 60646-35-7.

References and Notes

(1) (a) The assignment of absolute configuration of γ-lactones has met with some success by the use of circular dichroism (CD).[1b] Beecham[1c] found a relationship between the sign of the n–π* absorption band and the configuration about the α-carbon atom for a series of γ-lactones. The magnitude and sign of the CD appeared to be independent of ring substitution in other positions. Kuriyama[1d] noted a correlation between chirality at the γ-carbon atom of some α,β-unsaturated γ-lactones and the sign of the π–π* Cotton effect. (b) For a brief review see A. F. Beecham, *Tetrahedron Lett.*, 3591 (1968). (c) A. F. Beecham, *ibid.*, 2355 (1968). (d) I. Uchida and K. Kuriyama, *ibid.*, 3761 (1974).

(2) The use of an NMR method giving distinguishable enantiomeric resonances has other inherent advantages over polarimetric methods for determination of enantiomeric composition. For example, for compounds of low specific rotation, typical of lactones of type **5** and **6**, small amounts of optically active impurities can cause errors in polarimetrically determined optical purities with misleading consequences. [For an example see T. Hiyama, T. Mishima, H. Sawada, and H. Nozaki, *J. Am. Chem. Soc.*, **98**, 641 (1976)].

(3) *Sense of nonequivalence* is defined as the field position of a particular signal of the major enantiomer relative to that of the minor enantiomer and is referred to as high field or low field.

(4) Models of the carbinol–substrate interaction causing this nonequivalence have been proposed for (a) aromatic amines, W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, 5849 (1968); (b) amino esters, W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **91**, 5150 (1969); (c) aryl amine oxides, W. H. Pirkle, R. L. Muntz, and I. C. Paul, *ibid.*, **93**, 2817 (1971); (d) sulfoxides, W. H. Pirkle, S. D. Beare, and R. L. Muntz, *Tetrahedron Lett.*, 2295 (1974); and (e) sulfinates, W. H. Pirkle and M. S. Hoekstra, *J. Am. Chem. Soc.*, **98**, 1832 (1976).

(5) (a) Electron densities at the carbonyl and ring oxygens of **5a** have been calculated[5b] to be 1.482 and 0.893, respectively. Infrared evidence of hydrogen bonding of adenine, uracil derivatives, and *N*-methylacetamide to some γ-lactones at the carbonyl oxygen has been presented.[5c] Furthermore, we find that addition of the shift reagent Eu(fod)$_3$ to carbon tetrachloride solutions of **7** or **8** induces much greater chemical shifts for the protons on the α carbons than for those in the γ position. This indicates coordination of the Eu(fod)$_3$ to the carbonyl oxygen. (b) H. G. Raubenheimer and D. H. DeKock, *J. S. Afr. Chem. Inst.*, **25**, 70 (1972). (c) *ibid.*, **25**, 321 (1972).

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(7) It should be recognized that these chemical shift generalizations are possible for γ-lactones since the latter are relatively planar. These generalizations may not hold for relatively nonplanar lactones even though the fundamental postulates of the model are sound. In such instances, lactone conformation must be considered when determining the relationship between stereochemistry and chemical shift pertubation.

(8) Pertinent NMR studies of the effects of epoxide rings on the chemical shifts of neighboring protons include K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 559 (1964); K. Tori and T. Komeno, *ibid.*, 1157 (1974); D. R. Paulson, F. Y. N. Tang, G. F. Moran, A. S. Murray, B. P. Pelka, and E. M. Vasquez, *J. Org. Chem.*, **40**, 184 (1975); S. G. Davies and G. H. Witham, *J. Chem. Soc., Perkin Trans. 2*, 861 (1975).

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The Facile, Regiospecific Protonation of Alkenes. A Model System

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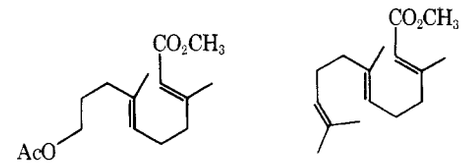
The protonation of olefins generally is accomplished only by relatively strong acids; in contrast, the enzymic protonation of a double bond presumably takes place under much milder conditions. Toward understanding of the mechanisms by which the latter can occur, it is of interest to examine chemical systems in which unusually facile double bond protonation takes place. We report herein such an example which we have uncovered.

To investigate the stability of *E*-α,β-unsaturated methyl esters with respect to double bond isomerization in acidic media,[2] **1** and **2** were treated with 85% phosphoric acid at room

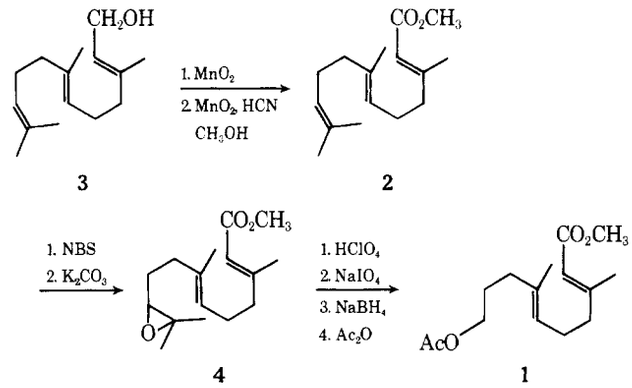


1 **2**

temperature. In contrast to compound **2**, which was recovered unchanged after 30 min, compound **1** underwent rapid and complete transformation. For this study, *E,E*-**1** was prepared stereospecifically, as described below.

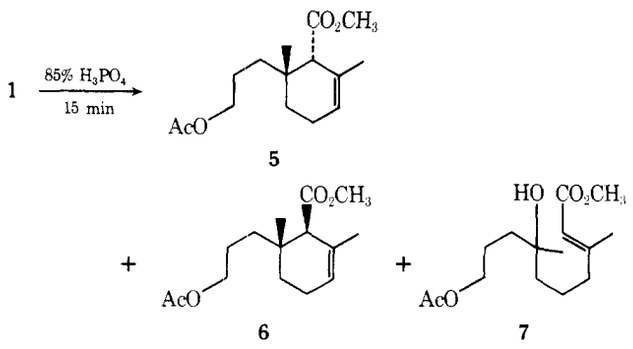
Utilizing active MnO_2 as the oxidant, transformation of (*E,E*)-farnesol (**3**) into **2** was accomplished via the corresponding aldehyde following the two-step procedure developed by Corey.[3] Silica gel chromatography afforded the analytically pure methyl ester with >98% isomeric purity. The ester **2** was then selectively epoxidized to give the known epoxy ester **4** using van Tamelen's NBS reaction, followed by treatment with base.[4] Epoxide **4** was transformed into the desired acetoxy ester **1** by standard means as outlined in Scheme I.

Scheme I



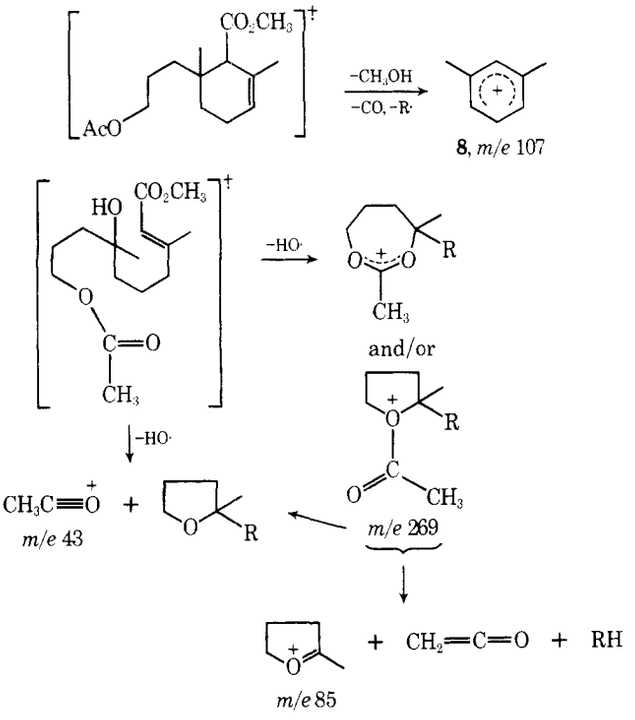
Dissolution of compound **1** for 15 min in 85% phosphoric acid at room temperature resulted in the formation of three major products, as determined by TLC (R_f 0.41, 0.36, 0.04; 5% ethyl acetate in benzene). Separation of these by silica gel chromatography and spectroscopic characterization showed them to be the cyclized epimers **5** and **6** and the acyclic, tertiary alcohol **7** (yields of 45% for **5** and **6** and 38% for **7**). The structural assignments were made on the basis of spectrometric properties. Thus, the NMR spectra of **5** and **6** each show an unsplit methyl at 0.88 ppm, a broadened, vinylic

Scheme II



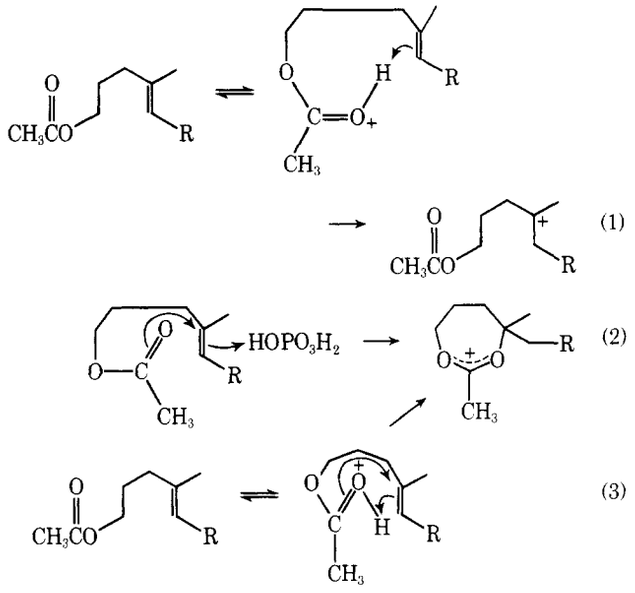
methyl at 1.61 ppm, and only one vinylic proton, as a poorly resolved multiplet at 5.55 ppm, in addition to the other appropriate signals. The mass spectrum of either epimer shows only a small molecular ion, but a base peak at *m/e* 107, formally corresponding to loss of CH_3OH, CO, and the alkyl side chain, forming the highly stabilized carbonium ion **8**. Compound **7** also is easily characterized by its spectral behavior: the IR spectrum shows the hydroxyl group at 3475 cm^{-1}, in addition to the acetate (1740 cm^{-1}) and unchanged α,β-unsaturated ester (1720 and 1650 cm^{-1}); the NMR spectrum, in addition to the signals characteristic of the functionality unchanged from compound **1**, shows an unsplit methyl group at 1.12 ppm and only one vinylic proton (5.63 ppm); finally, the mass spectrum contains no molecular ion, a small peak at *m/e* 269 (M − OH), *no* peak at *m/e* 268 (M − H_2O), a base peak at *m/e* 43 (acetyl), and a characteristic peak at *m/e* 85; these fragments, and lack of a molecular ion, can be rationalized as shown in Scheme III.

Scheme III



In spite of the demonstrated stability of similar olefins, such as **2**, toward direct double bond protonation under these conditions, products **5**, **6**, and **7** all have arisen as the result of rapid, regiospecific protonation of the 6,7 double bond, thereby (formally) forming a carbonium ion at C-7, which then is subject to nucleophilic attack. Additional experiments have provided some evidence regarding plausible causes for this observed selectivity. Thus, when the concentration of compounds **1** and **2** in 85% phosphoric acid is tenfold lower, compound **1** still is protonated exclusively. This suggests that the selectivity is not simply due to solubility differences. Further, no reaction occurs when either compound **1** or **2** is treated with (1) 50% phosphoric acid, (2) glacial acetic acid, or (3) a 30:70 mixture of 85% phosphoric acid and glacial acetic acid. These experiments indicate that the selective protonation of **1** arises from the special, highly ionizing, nonnucleophilic properties[5] of 85% phosphoric acid, probably coupled with some manner of participation by the acetoxy group. Mechanisms for involvement of the acetoxy group which we consider plausible are shown in Scheme IV: (1) intramolecular protonation of the

Scheme IV



double bond by the protonated acetoxy group,[6] (2) stabilization of the carbonium ion (and the transition state leading to it) by the acetoxy carbonyl group, and (3) a combination of these two alternatives, effectively a 1,2 addition to the double bond.[7] Possible underlying mechanistic parallels between this reaction and other examples[8] of chemical, regiospecific protonation of olefins suggest that further study of these systems is warranted.

Experimental Section

Gas chromatographic separations were performed on a 6-ft column packed with 4% OV-101 on high performance Chromosorb G. For TLC and column chromatography, Merck $HF_{254/366}$ and Merck PF_{254} silica gel were used, respectively. Elemental analyses were run by Galbraith Laboratories, Inc.

***(E,E)*-Methyl Farnesate 10,11-Oxide (4).**[9] To 314 mg (1.26 mmol) of (*E,E*)-methyl farnesate[10] (**2**) in 16 ml of *tert*-butyl alcohol and 21 ml of H_2O at ca 10 °C was added with stirring under N_2 235 mg (1.32 mmol) of *N*-bromosuccinimide (recrystallized from H_2O). After the reaction mixture was stirred for 80 min without further cooling, most of the solvent was removed under reduced pressure, and the remaining mixture was saturated with NaCl and extracted (3 × 15 ml of diethyl ether). The ether solution was dried ($MgSO_4$), filtered, and concentrated, affording 403 mg of crude bromohydrin **9** as an oil.

To 390 mg (1.12 mmol) of **9** in 15 ml of CH_3OH was added 387 mg of anhydrous K_2CO_3 and the resulting mixture was stirred for 30 min, after which 30 ml of diethyl ether and 30 ml of H_2O were added. The aqueous portion was extracted (3 × 30 ml of pentane), and the combined organic portions were washed (2 × 50 ml of saturated aqueous NaCl), dried ($MgSO_4$), filtered, and concentrated to give 294 mg of crude epoxide. Chromatographic purification (15 g of silica gel, 12% ethyl acetate/hexane) of 284 mg afforded 201 mg of pure epoxide **4** (60%): TLC (20% ethyl acetate/hexane) R_f 0.56; IR (neat) 1720 (C=O) and 1650 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 5.63 (s, 1, C=C**H**CO_2CH_3), 5.17 (broad s, 1, C=C**H**), 3.63 (s, 3, CO_2CH_3), 2.52 (t, 1, J = 6 Hz, OCH), 2.17 (s, CH_3C=CHCO$_2$), 1.63 (CH_3C=CH), and 1.21 and 1.23 ppm [s, 6, $(CH_3)_2$C]; mass spectrum (70 eV) *m/e* (rel

intensity) 266 (1), 123 (56), 109 (30), 102 (48), 95 (30), 83 (31), 81 (36), 73 (33), 70 (40), 69 (100), 59 (53), 57 (38), 43 (35), 31 (54), 29 (38).

(*E,E*)-Methyl 10-Acetoxy-3,7-dimethyl-2,6-decadienoate (1). To 194 mg (0.73 mmol) of epoxide **4** in 15 ml of tetrahydrofuran and 15 ml of H_2O was added with rapid stirring at room temperature 0.15 ml (0.08 mmol) of 3% $HClO_4$. After the reaction mixture was stirred for 23 h, NaCl was added to saturation, the aqueous portion was extracted (3 × 25 ml of diethyl ether), and the combined organic portions were washed (2 × 15 ml of saturated aqueous NaCl), dried ($MgSO_4$), filtered, and concentrated to give 222 mg of crude glycol (**10**): TLC (50% ethyl acetate/hexane) R_f 0.35; IR (neat) 3425 cm^{-1} (OH); NMR (CCl_4) δ 1.08 ppm [s, 6, $(CH_3)_2COH$]; mass spectrum (70 eV) *m/e* (rel intensity) 284 (6), 81 (63), 59 (52), 43 (100), 41 (56).

To 210 mg (0.74 mmol) of glycol **10** in 10 ml of tetrahydrofuran and 10 ml of H_2O was added 444 mg (2.07 mmol) of $NaIO_4$. After the reaction mixture was stirred for 3 h, NaCl was added to saturation, the layers were separated, the aqueous portion was extracted (1 × 10 ml of pentane, 3 × 10 ml of diethyl ether), and the combined organic portions were washed (2 × 15 ml of H_2O, 1 × 25 ml of saturated aqueous NaCl), dried ($MgSO_4$), and concentrated, affording 158 mg of crude aldehyde (**11**): TLC (20% ethyl acetate/hexane) R_f 0.38; IR (neat) 2725 cm^{-1} (CHO); NMR (CCl_4) δ 9.77 ppm (s, 1, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 224 (6), 114 (52), 93 (100), 85 (54), 55 (79).

To 150 mg (0.67 mmol) of aldehyde **11** in 20 ml of CH_3OH was added 14 mg (0.37 mmol) of $NaBH_4$, and the resulting mixture was stirred for 20 min, at which time 1 ml of 2% HCl was added and most of the solvent was removed under reduced pressure. To the remaining mixture was added 25 ml of diethyl ether and 25 ml of H_2O, the layers were separated, the aqueous portion was extracted (3 × 15 ml of diethyl ether), and the combined organic portions were washed (1 × 15 ml of 10% $NaHCO_3$, 2 × 15 ml of saturated aqueous NaCl), dried ($MgSO_4$), and concentrated, affording 149 mg of hydroxy ester (**12**): TLC (20% ethyl acetate/hexane) R_f 0.17; IR (neat) 3400 cm^{-1} (OH); NMR (CCl_4) δ 3.51 ppm (t, 2, J = 6 Hz, CH_2OH); mass spectrum (70 eV) *m/e* (rel intensity) 226 (5), 114 (52), 95 (100), 85 (56).

To 146 mg (0.65 mmol) of hydroxy ester **12** in 0.5 ml of pyridine was added 0.5 ml of acetic anhydride, and the resulting mixture was stirred for 23 h, at which time the volatile material was removed under reduced pressure. The remaining oil was dissolved in 25 ml of diethyl ether and the resulting solution was washed (2 × 10 ml of 2% HCl, 1 × 10 ml of 10% $NaHCO_3$, 1 × 10 ml of H_2O, 1 × 10 ml of saturated aqueous NaCl), dried ($MgSO_4$), and concentrated, affording 154 mg of crude acetoxy ester **1**, crude yield 57% based on epoxide **4**. Silica gel chromatography (27 g, 8% ethyl acetate/hexane) of 450 mg of material so obtained provided 335 mg of purified **1**: TLC (20% ethyl acetate/hexane) R_f 0.46; UV max (95% ethanol) 218 nm (ϵ 6700); IR (neat) 1740 (acetate C=O), 1720 (ester C=O), and 1650 cm^{-1} (C=C); NMR (CCl_4) δ 5.64 (s, 1, $CHCO_2CH_3$), 5.14 (broad t, 1, J = 7 Hz, CH=CCH_3), 3.98 (t, 2, J = 6 Hz, $CH_3CO_2CH_2$), 3.64 (s, 3, CO_2CH_3), 2.17 [s, $C(CH_3)$=$CHCO_2CH_3$], 1.99 (s, CH_3CO_2), and 1.64 ppm [s, $C(CH_3)$=$CHCH_2$]; mass spectrum (70 eV) *m/e* (rel intensity) 268 (3), 114 (33), 95 (100). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.86; H, 8.95.

Treatment of (*E,E*)-Methyl 10-Acetoxy-3,7-dimethyl-2,6-decadienoate with 85% H_3PO_4. To 206 mg (0.77 mmol) of acetoxy ester **1** was added 17 ml of 85% H_3PO_4 (Mallinkrodt, AR) and the resulting homogeneous orange solution was stirred for 15 min, at which time 170 ml of H_2O was added. The resulting mixture was extracted (3 × 50 ml of diethyl ether) and 25 ml of saturated aqueous NaCl added to the aqueous portion, which was then extracted again (1 × 50 ml of diethyl ether). The combined organic portions were washed (1 × 50 ml of saturated aqueous $NaHCO_3$, 1 × 50 ml of saturated aqueous NaCl), dried ($MgSO_4$), filtered, and concentrated, affording 195 mg of an oil. Silica gel chromatography (14 g, 2% ethyl acetate/benzene) afforded 81 mg (42%) of purified epimers **5** and **6** total. Additional elution (ethyl acetate) afforded 71 mg (37%) of tertiary alcohol **7**.

Epimers **5** and **6** were obtained in three fractions, two (55 and 17 mg) of which each contained only one stereoisomer; the middle faction (9 mg) contained a mixture of the two. They are characterized by chromatography: TLC (5% ethyl acetate/hexane) R_f 0.41 (major) and 0.36 (minor) (acetoxy ester **1**, R_f 0.41); GC (100 °C, rising to 200 °C at 6 °C/min) retention times 29.2 min for both epimers and 37.2 min for acetoxy ester **1**. The spectral and analytical behaviors of the two epimers were essentially the same: UV max (95% ethanol) 218 nm (ϵ 5600); IR (neat) 1735 cm^{-1} (ester and acetate C=O); NMR (CCl_4) δ 5.57 (m, 1, C=CH), 3.99 (t, 2, J = 7 Hz, $CH_3CO_2CH_2$), 3.67 (s, 3, CO_2CH_3), 2.63 (s, 1, $CHCO_2CH_3$), 1.99 (s, CH_3CO_2), 1.63 (s, C=CCH_3), and 0.92 ppm (s, 3, CCH_3); mass spectrum (70 eV) *m/e* (rel intensity) 268 (1), 236 (23), 205 (26), 192 (31), 149 (41), 148 (38), 107 (100), 95 (52), 93 (45), 91 (41), 67 (38), 43 (72), 41 (35). Anal Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.33; H, 9.11.

An analytically pure sample of tertiary alcohol **7** was obtained by column chromatography (7 g of silica gel, 20% ethyl acetate/benzene): TLC (25% ethyl acetate/benzene) R_f 0.23; GC (100 °C, rising to 200 °C at 6 °C/min) retention time 53 min; UV max (95% ethanol) 218 nm (ϵ 1800); IR (CCl_4) 3475 (OH), 1740 (acetate C=O), 1720 (ester C=O), and 1650 cm^{-1} (C=C); NMR (CCl_4) δ 5.63 (s, 1, C=$CHCO_2$), 4.02 (t, 2, J = 6 Hz, $CH_3CO_2CH_2$), 3.63 (s, 3, CO_2CH_3), 2.13 (d, J = 1 Hz, C=CCH_3), 1.99 (s, CH_3CO_2), and 1.12 ppm (s, 3, $HOCCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 269 (<1), 153 (31), 114 (28), 107 (26), 95 (48), 85 (62), 43 (100). Anal. Calcd for $C_{15}H_{26}O_5$: C, 62.91; H, 9.15. Found: C, 62.78; H, 9.12.

Determination of Yields of 4-(γ-Acetoxypropyl)-3-carbomethoxy-2,4-dimethylcyclohexenes (5 and 6) and (*E*)-Methyl 10-Acetoxy-7-hydroxy-3,7-dimethyldecenoate (7) by GC. According to the procedure described above, 10.06 mg (0.038 mmol) of acetoxy ester **1** was treated with 0.8 ml of 85% H_3PO_4. After workup the resulting diethyl ether solution was diluted to 25.0 ml and a 1.00-ml aliquot was removed. To the remaining 24 ml was added 2.40 mg (0.009 mmol) of acetoxy ester **1** as an internal standard. GC analysis as above showed no remaining acetoxy ester **1** in the reaction mixture. Using compound **1** as an internal standard, the yields of cyclized epimers **5** and **6** were determined to be 45% (ca 3:1 ratio, by TLC) and of tertiary alcohol **7** to be 38%.

Treatment of Methyl Farnesate[11] (2) with 85% Phosphoric Acid. To 2.61 mg (0.0086 mmol) of **2** was added 0.14 ml (2.23 mmol) of 85% H_3PO_4 and the resulting mixture was stirred at room temperature for 30 min, at which time 1.4 ml of water was added. The reaction mixture was extracted (3 × 1 ml of diethyl ether), and 1 ml of saturated aqueous NaCl was added to the aqueous portion, which was then extracted again (1 × 1 ml of diethyl ether). The combined organic portions were washed (2 × 1 ml of saturated aqueous $NaHCO_3$, 1 × 1 ml of saturated aqueous NaCl), dried ($MgSO_4$), and filtered; GC showed unreacted **2** to be the only compound present.

Treatment of Methyl Farnesate[11] (2) and (*E,E*)-Methyl 10-Acetoxy-3,7-dimethyl-2,6-decadienoate (1) with 85% Phosphoric Acid at Tenfold Dilution. To 2.38 mg (0.0095 mmol) of **2** and 2.24 mg (0.0084 mmol) of **1** was added 2.8 ml (44.54 mmol) of 85% H_3PO_4 and the remaining mixture was stirred at room temperature for 15 min, at which time 28 ml of H_2O was added. The reaction mixture was extracted (3 × 10 ml of diethyl ether) and 10 ml of saturated aqueous NaCl was added to the remaining aqueous portion, which was then extracted again (2 × 10 ml of diethyl ether). The combined organic portions were washed (2 × 10 ml of saturated aqueous $NaHCO_3$, 1 × 10 ml of saturated aqueous NaCl), dried ($MgSO_4$), and filtered; GC showed **2** to be completely unreacted and **1** transformed entirely into **5, 6,** and **7**.

Treatment of Methyl Farnesate[11] (2) and (*E,E*)-Methyl 10-Acetoxy-3,7-dimethyl-2,6-decadienoate (1) with 50% Phosphoric Acid. To 2.24 mg (0.0089 mmol) of **2** and 2.47 mg (0.0092 mmol) of **1** was added 0.49 ml (4.59 mmol) of 50% H_3PO_4 and the resulting mixture was stirred at room temperature for 15 min, at which time 4.9 ml of H_2O was added. The reaction mixture was extracted (4 × 1 ml of diethyl ether), and 1 ml of saturated aqueous NaCl was added to the remaining aqueous portion which was then extracted again (2 × 1 ml of diethyl ether). The combined organic portions were washed (2 × 1 ml of saturated aqueous $NaHCO_3$, 1 × 1 ml of saturated aqueous NaCl), dried ($MgSO_4$), and filtered; GC showed only unreacted **2** and **1** to be present.

Treatment of Methyl Farnesate[11] (2) and (*E,E*)-Methyl 10-Acetoxy-3,7-dimethyl-2,6-decadienoate (1) with Glacial Acetic Acid. To 4.19 mg (0.017 mmol) of **2** and 4.68 mg (0.017 mmol) of **1** was added 2.00 ml (34.86 mmol) of CH_3CO_2H and the resulting mixture was stirred at room temperature for 45 min, at which time 20 ml of H_2O was added. The reaction mixture was extracted (3 × 10 ml of diethyl ether), and 10 ml of saturated aqueous NaCl was added to the remaining aqueous portion, which was then extracted again (2 × 10 ml of diethyl ether). The combined organic portions were washed (2 × 10 ml of saturated aqueous $NaHCO_3$, 1 × 10 ml of saturated aqueous NaCl), dried($MgSO_4$), and filtered; GC showed only unreacted **2** and **1** to be present.

Treatment of Methyl Farnesate[11] (2) and (*E,E*)-Methyl 10-Acetoxy-3,7-dimethyl-2,6-decadienoate (1) with a 30:70 Mixture of 85% Phosphoric Acid and Glacial Acetic Acid. To 1.07 mg (0.0043 mmol) of **2** and 1.23 mg (0.0046 mmol) of **1** was added 0.40 ml (0.0068 mmol) of a 30:70 mixture of 85% H_3PO_4–CH_3CO_2H and the resulting mixture was stirred at room temperature for 1 min, at which time 4 ml of H_2O was added. The reaction mixture was extracted (3

× 1 ml of diethyl ether), and 1 ml of saturated aqueous NaCl was added to the remaining aqueous portion, which was then extracted again (2 × 1 ml of diethyl ether). The combined organic portions were washed (2 × 1 ml of saturated aqueous $NaHCO_3$, 1 × 1 ml of saturated aqueous NaCl), dried ($MgSO_4$), and filtered; GC showed only unreacted **2** and **1** to be present.

Registry No.—**1**, 60718-74-3; **2**, 3675-00-1; **4**, 5299-11-6; **5**, 60718-75-4; **6**, 60718-76-5; **7**, 60718-77-6; **9**, 60718-78-7; **10**, 36999-94-7; **11**, 38227-49-5; **12**, 60718-79-8; *N*-bromosuccinimide, 128-08-5; H_3PO_4, 7664-38-2; acetic acid, 64-19-7.

References and Notes

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(9) E. J. Hessler, Ph.D. Thesis, Stanford University, Stanford, Calif., 1964.
(10) Prepared according to the described[3] procedure and purified by chromatography on silica gel (2% ethyl acetate/hexane); GC analysis (170 °C, 4 °C/min increase, retention time, 15.1 min) indicated greater than 98% isomeric purity.
(11) A mixture (ca. 85:15) of *E,E* and *Z,E* isomers, by GC.

On the Transformation of Benzoin to Tetraphenylfuran in the Presence of *p*-Toluenesulfonic Acid in Boiling Xylene

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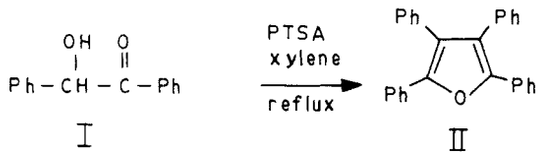
Benzoin (I) is known to undergo an interesting transformation to tetraphenylfuran (II) when refluxed with *p*-toluenesulfonic acid (PTSA) in dry xylene with azeotropic removal of water. This observation, originally made by Berger and Summerbell,[2] is still the best method for making II:[3,4]

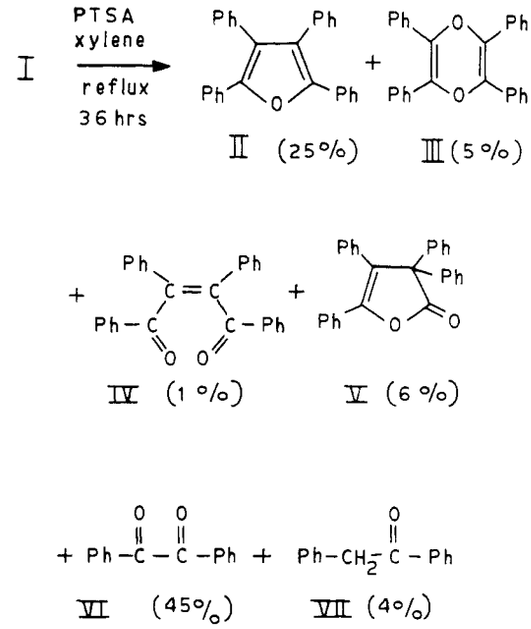


I II

Owing to the simplicity of the reaction and its possible potentiality of opening up of a novel route for the synthesis of furans, the present study was undertaken. In our hands benzoin (I), when refluxed under identical conditions, besides giving II, yielded five more compounds, namely, tetraphenyl-1,4-dioxadiene (III),[2] *cis*-dibenzoylstilbene (IV),[5] tetraphenyllactone (V),[6] benzil (VI),[7] and deoxybenzoin (VII),[8] all of which were identified by comparison with authentic compounds.

Table I. Yields of the Products Obtained in Different Reactions of I (%)

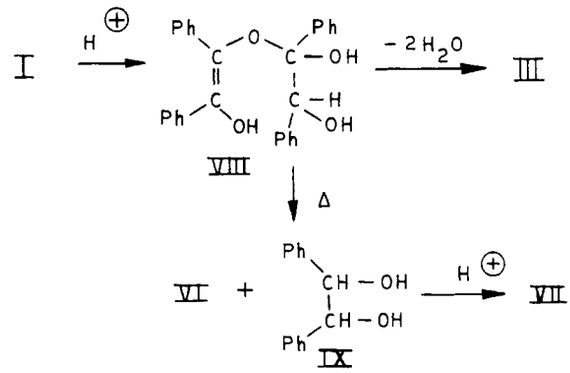
Reaction	II	III	IV	V	VI	VII
1	25.0	5.0	1.0	6.0	45.0	4.0
2	26.0	8.0	2.5	9.0	45.0	5.0
3	30.0	5.0	5.0	9.0	46.0	3.0
4	13.0	3.0	3.0	30.0	23.0	3.0



Slightly enhanced yields of all the products were obtained when an equimolar mixture of benzoin and benzoin acetate[9] was refluxed in dry xylene under identical conditions. With deoxybenzoin (VII) added to the reaction mixture yields of the furan (II), *cis*-dibenzoylstilbene (IV), and the lactone (V) increased appreciably.

Similarly when *cis*-dibenzoylstilbene (IV) was added to the reaction mixture the lactone (V) was obtained in higher yields. On the basis of all these observations (Table I) and other related evidences we have rationalized the transformation of benzoin (I) to the observed products in the following manner.

In the presence of acid benzoin (I) undergoes a self-condensation reaction giving rise to the intermediate VIII which then can form III, VI, and VII as follows.



The formation of tetraphenylfuran (II) in this reaction has to involve the condensation of two species forming a carbon–carbon bond and it is quite likely that deoxybenzoin (VII) formed in this reaction condenses with benzoin in the presence of acid to give the intermediate X which could ultimately yield