is formed in the reaction of 1 with the thiolate ion. In fact, since the thiolate ion is more polarizable than methoxide ion, the corresponding transition state for the formation of the intermediate σ adduct should be looser with thiolate ion than with methoxide ion, and therefore steric effects should be less important in the former.

Kinetic and activation data for the methoxy denitration of 1 are reported in Table I, together with related literature data for the methoxy denitration of 1-methyl-2,5-dinitropyrrole and *o*- and *p*-dinitrobenzene. These data show that the reactivity of the 2,3-dinitropyrrole derivative is lower by a factor of 3.4 than the reactivity of the 2,5-dinitropyrrole derivative. This behavior is similar to that of the related *o*- and *p*-dinitrobenzene in the same reaction, which shows a lower reactivity of the ortho derivative by a factor of 2.4.

In the methoxy denitration reaction the dinitropyrrole derivatives tested so far are nearly 1 order of magnitude more reactive that the corresponding benzene derivatives. The activation data are not very different and cannot give an unequivocal interpretation of the small rate differences observed in the methoxy denitration reaction. However, it can be observed that the reactions of the ortho-like compounds are characterized by a more negative activation entropy, which seems to be the more significant factor in determining the reactivity order between ortho- and para-like compounds.

Experimental Section

Melting points are uncorrected. ^{1}H NMR measurements were carried out with a WP 80 SY Bruker spectrometer, unless otherwise stated. Mass spectra were obtained with a VG 7070F instrument. The kinetic measurements were carried out spectrophotometrically in the thermostated cell compartment of a Cary 219 instrument. An excess of sodium methoxide was present, so that the reactions occurred under pseudo-first-order conditions. The kinetics were followed at the wavelength corresponding to the largest absorbance change in going from 1 to the substitution product (250 nm). Owing to the high methoxide ion concentration, the ionic strength was kept constant by adding $NaClO_4$.

1-Methyl-2,3-dinitropyrrole (1) was prepared by dinitration of 1-methylpyrrole and separated from its isomers according to a described procedure.[10]

2-Methoxy-1-methyl-3-nitropyrrole (2). Sodium methoxide (0.44 mol) was added to a solution of 1 (0.20 g, 0.11 mol) in 5 mL of methanol kept at 45 °C. After 90 min the excess of sodium methoxide was neutralized with dilute HCl. The solution was repeatedly extracted with ethyl ether. The ether solution was dried and evaporated to yield 0.17 g (yield 93%) of a white solid: mp (CCl_4) 82–82.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3 H, NCH_3), 4.10 (s, 3 H, OCH_3), 6.17 (d, 1 H, J = 3.9 Hz); 6.57 (d, 1 H, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 31.8 (NCH_3), 62.5 (OCH_3), 103.7 (C-4), 113.7 (C-5), 121.9 (C-3), 145.3 (C-2); UV (MeOH) λ_{max} 278, 334 nm; mass spectrum, calcd for $C_6H_8N_2O_3$ (M^+) m/e 156.05354, found 156.0538.

Nitration of 2 was carried out at 0 °C by adding 1 mL of a nitrating mixture (made up from 0.5 mL of 90% HNO_3 and 20 mL of acetic anhydride) to a solution of 80 mg of 2 in 5 mL of acetic anhydride. After 4 h the reaction mixture was poured into water and, after hydrolysis of the anhydride, extracted with ethyl ether (4 × 50 mL). The ether extracts were washed with a saturated $NaHCO_3$ solution, water, and finally dried (Na_2SO_4). The residue after evaporation of the solvent was chromatographed (silica gel, 9:1 benzene–ethyl acetate) to yield 30 mg of 2-methoxy-1-methyl-3,5-dinitropyrrole (mp 85–86 °C, lit.[7] 86–86.5 °C) together with some unreacted 2.

Reaction of 1 with Sodium *p*-Methylbenzenethiolate. Sodium methoxide (0.38 mL of a 4.64 M methanol solution) was added to a solution of 0.3 g of 1 and 0.27 g of *p*-methylbenzenethiol kept at 30 °C. After 10 min the reaction was complete. TLC analysis (silica gel, benzene) showed the presence of two compounds that were separated chromatographically (Merck 10401 Lichroprep Lobar, 4:1 benzene–ethyl acetate). The main product (0.375 g, yield 86%) was eluted first: mp 110–110.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H, Me-Ar), 3.62 (s, 3 H, MeN), 6.77 (d, 1 H, J = 3.32 Hz), 6.90 (d, 1 H, J = 3.32 Hz), 7.07 (pseudo-s, 4 H, (C_6H_4)); ^{13}C NMR ($CDCl_3$) δ 20.8 (MeAr), 35.2 (MeN), 128.1, 130.1, 130.9, 136.9 for the benzene ring, 106.9 (pyrrole C-4), 121.8 (pyrrole C-3), 123.8 (pyrrole C-5), 139.0 (pyrrole C-2); UV (MeOH) λ_{max} 238 nm; mass spectrum, calcd for $C_{12}H_{12}N_2O_2S$ (M^+) m/e 248.06206, found 248.0592.

The minor isomer (4 mg, yield 0.9%) did not lend itself to further purification and was characterized only through the following features: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.39 (s, 3 H), 3.97 (d, 1 H, J = 0.45 Hz), 5.46 (d, 1 H, J = 2.96 Hz), 6.65 (dd, 1 H, J = 0.45, 2.96 Hz), 7.25 (d, 2 H, J = 8.1 Hz), 7.50 (d, 2 H, J = 8.1 Hz); mass spectrum (M^+), m/e 248.

The structural assignment to the products of *p*-methylbenzenethiolate denitration was based upon the fact that both substitution products display a coupling constant which is in agreement with a 2,3-disubstitution pattern.[10] Moreover, the α hydrogen differs from the β hydrogen because of a weak coupling (nearly 0.5 Hz) which is usually responsible for a lower resolution in the former signal. This fact allows an easy identification of the substitution pattern when the effect of the substituents is considered.

Acknowledgment. We thank Prof. G. Illuminati for helpful discussions, and Dr. Anna Maria Giuliani and E. Brancaleoni (CNR Area delle Ricerche, Roma, Italy) for the ^{13}C NMR spectra and high-resolution mass spectra.

Registry No. 1, 72795-78-9; 2, 101493-73-6; 2-methoxy-1-methyl-3,5-dinitropyrrole, 89998-66-3; 1-methyl-2-((4-methylphenyl)thio)-3-nitropyrrole, 101493-74-7; *p*-methylbenzenethiol, 106-45-6.

(10) Grehn, L. *Chem. Scr.* **1978**, *13*, 67.

Regioselective Conversion of Allylic Alcohols to 1-Propenes via Organoiron Complexes

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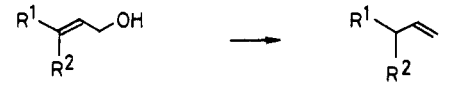
Regioselective reduction of 2-propen-1-ols (allylic alcohols) to 1-propenes with a transposition of the allylic double bond (eq 1) is an important process in synthetic



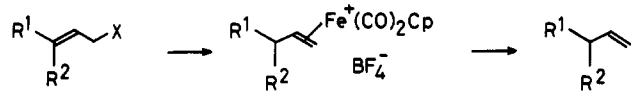
(1)

chemistry. Recent development of this reaction involves the lithium aluminum hydride reduction of allylic phosphonates[1] and triphenylphosphonium salts[2] and protolysis of allylic stannanes,[3] which are derived from allylic alcohols. We describe here a general method for this purpose which utilizes the characteristics of iron carbonyl complexes.[4] This process involves the successive transformation of allylic alcohols 1, via allylic phosphates 2, (η^1-allyl)$Fe(CO)_2Cp$ (3), and (η^2-olefin)$Fe(CO)_2Cp$ complexes 4 to 1-propenes 5 (Scheme I). As an application of the

(1) Kondo, K.; Negishi, A.; Tunemoto, D. *Angew, Chem.* **1974**, *86*, 415. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 407.
(2) Hirabe, T.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1984**, *49*, 4084.
(3) Ueno, Y.; Sano, H.; Okawara, M. *Tetrahedron Lett.* **1980**, *21*, 1767.
(4) For reviews see: (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Birch, A. J.; Jenkins, I. D. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976.

0022-3263/86/1951-2126$01.50/0

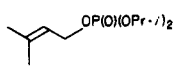
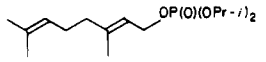
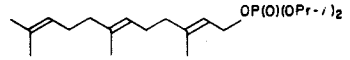
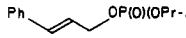
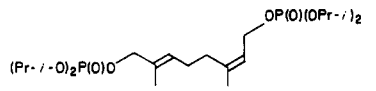
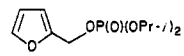
Scheme I



1 X = OH
2 OP(O)(OPr^i)$_2$
3 Fe(CO)$_2$Cp

4 5

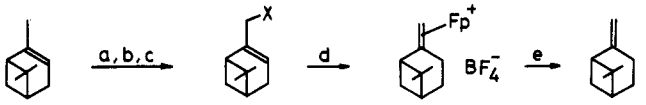
Table I. Yields of (η^1-Allyl)Fp 3 and (η^2-Olefin)Fp$^+$BF$_4^-$ 4

entry	phosphate 2	yield, % 3	4
a	 2a	79	69
b	 2b	79	71
c	 2c	63	67
d	 2d	74	57
e	 2e	49	33
f	 2f	79	0

present method, regioselective transformation of α-pinene to β-pinene is also described.

It has been reported that the reaction of NaFe(CO)$_2$Cp (NaFp) with allylic halides and sulfonates gives (η^1-allyl)Fp complexes.[5] We have found that allylic diisopropyl phosphates **2**, readily obtainable by the phosphorylation of allylic alcohols **1** with diisopropyl phosphorochloridate, also gave good yields of the (η^1-allyl)iron complexes **3**. As summarized in Table I, six kinds of allylic phosphate gave the respective (η^1-allyl)Fp complexes in 49–79% yields. The substitution occurred regiospecifically at the α-position of the allylic system (S_N2 reaction). Although the iron complexes **3** are air-sensitive, they were easily purified by column chromatography on alumina under nitrogen atmosphere, and the structures were deduced by the spectroscopic data. Protonation of the σ-complex **3** with tetrafluoroboric acid gave rise to the formation of the stable cationic π-complex, (η^2-olefin)FpBF$_4$ (**4**),[5] in good yields. The protonation of **3** is highly regioselective, exclusively giving the olefin complex **4** protonated at the γ-position of the allylic system. Evidence for the formation of α-protonated products was not observed. Yields of the cationic complexes prepared are summarized in Table I. Prenyl, geranyl, (*E*,*E*)-farnesyl, and (*E*)-cinnamyl derivatives (entry a–d) all gave good yields of the respective cationic complexes (**4a–d**). Diallylic compound (entry e) also gave the bis-Fp dication **4e**. However, the protonation of the furfuryl compound **3f** gave a complex mixture of products, from which the desired cationic complex **4f** could not be isolated.

Scheme II[a]



6 8 X = OH 9 OP(O)(OPr^i)$_2$ 10 Fp 11 7

[a] (a) *t*-BuOOH-SeO$_2$, 47%; (b) ClP(O)(O-*i*-Pr)$_2$-pyridine, 82%; (c) NaFp, 57%; (d) HBF$_4$, 100%; (e) NaI, 52%.

Finally, the treatment of **4** with sodium iodide resulted in smooth demetalation[6] to give 1-propenes **5**. For example, when the cationic complex **4b** was stirred with a slight excess of sodium iodide in acetone at 0 °C for 30 min, 3,7-dimethyl-1,6-octadiene was obtained in 56% isolated yield.

In order to demonstrate the synthetic utility of the present process, the transformation of α-pinene (**6**) to β-pinene (**7**) was achieved.[7] Myrtenol (**8**), prepared in 47% yield by the oxidation of α-pinene by using the Sharpless method,[8] was phosphorylated to the diisopropyl phosphate **9** in 82% yield. The reaction of **9** with NaFp gave (η^1-myrtenyl)Fp (**10**) as yellow crystals in 57% yield. Protonation of **10** with HBF$_4$ gave the cationic (η^2-β-pinene)Fp complex **11** quantitatively. Treatment of **11** with sodium iodide in acetone liverated β-pinene in 52% isolated yield. The demetalation process proceeded almost quantitatively; the low isolated yield is attributed to the high volatility of the product **17**. The obtained β-pinene was free from isomers. Thus, α-pinene was regioselectively converted to β-pinene in five steps in the overall yield of 11% (Scheme II).

The high selectivity and the mild reaction conditions of the present process provide a useful method for the conversion of allylic alcohols to 1-propenes.

Experimental Section

Melting points were determined with a hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a JASCO A-102 spectrometer. ^{1}H and ^{13}C NMR spectra were run with Hitachi R-24A (60 MHz) and Varian XL-200 (50 MHz) spectrometers, respectively. Elemental analyses were performed at the Elemental Analysis Center of Kyoto University.

Synthesis of Diisopropyl Myrtenyl Phosphate (9). To a solution of myrtenol (**8**) (1.58 g, 10.4 mmol) in pyridine (5 mL) was added dropwise diisopropyl phosphorochloridate[10] (2.5 g, 12.5 mmol) at 0 °C, and the mixture was stirred at 0 °C for 4 h. Cold water (30 mL) was added, and the product was extracted with ether. The extracts were successively washed with diluted (1 N) sulfuric acid, saturated aqueous sodium hydrogen carbonate, and brine and then dried (Na$_2$SO$_4$). The solvent was evaporated under reduced pressure to give the phosphate **9** (2.71 g, 82%). The product thus obtained was sufficiently pure and used without further purification: IR (neat) 1280, 1265, 1180, 1145, 1115, 1010 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 0.85 (s, 3 H, CH$_3$), 1.20–1.35 (m, 15 H, CH$_3$), 1.60–2.60 (m, 6 H, CH$_2$ and CH), 4.25 (d, J = 6 Hz, 2 H, OCH$_2$), 4.35–4.90 (m, 2 H, CH), 5.55 (br s, 1 H, olefin).

Synthesis of (η^1-Allyl)Fp Complexes 3a–f and 10. The following reaction of diisopropyl myrtenyl phosphate (**9**) with NaFp is representative. To a solution of NaFp, prepared from the reaction of Fp$_2$ (973 mg, 2.75 mmol) with sodium amalgam

(5) (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189. (b) Merour, J.-Y.; Cadiot, P. *C. R. Seances Acad. Sci., Ser. C* **1970**, *271*, 83. (c) Culter, A.; Ehntholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. (d) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291.

(6) Giering, W. P.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1972**, *94*, 7170. Rosan, A.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1973**, 95, 3062. Rosenblum, M.; Saidi, M. R.; Madhavarao, M. *Tetrahedron Lett.* **1975**, 4009.

(7) Examples of regioselective conversion of α-pinene to β-pinene are known: (a) Brown, H. C.; Bhatt, M. V. *J. Am. Chem. Soc.* **1960**, *82*, 2074. (b) Harwood, L. M.; Julia, M. *Synthesis* **1980**, 456.

(8) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526.

(9) Sosnovsky, G.; Zaret, E. H. *J. Org. Chem.* **1969**, *34*, 968.

in tetrahydrofuran (16 mL) according to the literature method,[5a,d] was added the phosphate **9** (1.62 g, 5.1 mmol) at −78 °C, and the mixture was stirred for 20 min at −78 °C and then 1 h at room temperature. The solvent was removed under reduced pressure, and the residue was washed several times with ether. The ether washings were dried over Na_2SO_4 and then column chromatographed on alumina (pentane–ether, 10:1) under nitrogen atmosphere. A yellow band was collected, and the solvent was evaporated to give yellow crystals of iron complex **10** (907 mg, 57%), mp 62–64 °C. The spectral data of this compound and other (η^1-allyl)Fp complexes (**3a–f**) are summarized in Table II in the supplementary material.

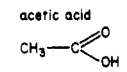
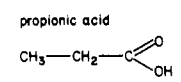
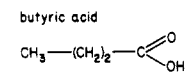
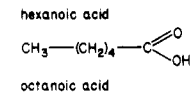
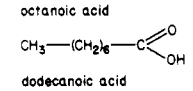
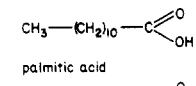
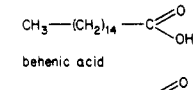
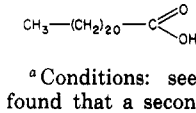
Protonation of (η^1-Allyl)Fp Complexes. Synthesis of (η^2-olefin)$Fp^+BF_4^-$ **4a–e** and **11**. The following reaction of **10** is representative. Complex **10** (421 mg, 1.35 mmol) was dissolved in a mixture of methanol (3 mL) and dichloromethane (3 mL). Tetrafluoroboric acid (42%, 0.22 mL, 1.62 mmol) diluted with methanol (1 mL) and dichloromethane (1 mL) was added over a period of 30 min, and the mixture was stirred for 2 h. Ice-water (30 mL) was added, and the mixture was extracted with dichloromethane. Dried over Na_2SO_4, the solvent was evaporated under reduced pressure to give a yellow solid. Recrystallization from dichloromethane–ether gave a yellow needles of complex **11** in quantitative yield. The melting points and the analytical and the spectral data of **11** and other (η^2-olefin)Fp cations **4a–e** are listed in Tables III and IV in the supplementary material.

Reaction of (η^2-β-Pinene)Fp^+ BF_4^- (11) with Sodium Iodide. To a solution of the cationic complex **11** (902 mg, 2.25 mmol) in acetone (18 mL) was added sodium iodide (405 mg, 2.7 mmol), and the mixture was stirred for 2 h in an ice bath. The solvent was then removed, and the black residue was chromatographed on silica gel with pentane as an eluate to give β-pinene in 52% yield. The product was identical (GLC and ^1H NMR) with an authentic sample obtained commercially.

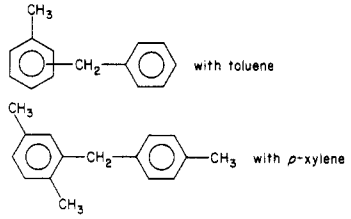
Registry No. **2a**, 83036-58-2; **2b**, 83036-59-3; **2c**, 101494-37-5; **2d**, 101494-38-6; **2e**, 101494-39-7; **2f**, 101494-40-0; **3a**, 38905-70-3; **3b**, 101494-26-2; **3c**, 101494-27-3; **3d**, 56389-66-3; **3e**, 101494-28-4; **3f**, 101494-29-5; **4a**, 89043-54-9; **4b**, 101494-31-9; **4c**, 101494-33-1; **4d**, 59980-55-1; **4e**, 101517-38-8; **6**, 80-56-8; **7**, 127-91-3; **8**, 515-00-4; **9**, 101494-41-1; **10**, 101494-34-2; **11**, 101494-36-4; $NaFe(CO)_2Cp$, 12152-20-4; $ClP(O)(O\text{-}i\text{-}Pr)_2$, 2574-25-5; 3,7-dimethyl-1,6-octadiene, 2436-90-0.

Supplementary Material Available: Physical properties, spectral data, and analyses for compounds prepared (6 pages). Ordering information is given on any current masthead page.

Table I. Acylation of Toluene and *p*-Xylene by Carboxylic Acids[a]

	aromatic compound				
	toluene				*p*-xylene
acylating agent	% yield (±2%) in acylated product[b]	isomers ortho	meta	para	% yield (±2%) in acylated product[b]
acetic acid 	ε[c]				ε[c]
propionic acid 	6	3	2	95	8
butyric acid 	20	3	2	95	22
hexanoic acid 	30	3	3	94	40
octanoic acid 	75	3	3	94	80
dodecanoic acid 	96	3	3	94	93
palmitic acid 	80	0.5	1	98.5	97
behenic acid 	55	0	0	100	60

[a] Conditions: see Experimental Section. [b] As expected, it was found that a secondary product, at a very low yield <1%, was formed, with toluene as well as with *p*-xylene, which results from dismutation of methyl benzenes.[8] ^{13}C NMR has provided convincing evidence for the structure assigned:



[c] It was verified that no side reaction occurs when the acylation reaction takes place partially, except the dismutation of methyl benzenes (see fnt *b*); the unreacting starting materials are fully recovered.

Friedel–Crafts Acylation of Toluene and *p*-Xylene with Carboxylic Acids Catalyzed by Zeolites

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The Friedel–Crafts reaction (alkylation and acylation of aromatic compounds) has been extensively studied in the past over various Lewis acid catalysts ($AlCl_3$, $FeCl_3$, $TiCl_4$)[1] and protonic acids (HF, H_2SO_4, HCl). Zeolites have received much attention recently in a wide range of contexts, particularly in the area of catalysis.[2] However, little attention has been given to the possibility of employing zeolites for promoting the Friedel–Crafts reaction.

Zeolites are salts of solid silicoaluminic acids characterized by a strictly regular structure of their crystalline lattice[3] and belonging to acid-type catalysts.[4] The acid form of zeolites is important in a variety of catalytic reactions including hydrocarbon cracking,[5] isomerization,[6] and alkylation.[7] These organic processes have been the subject of considerable interest during the last decade.

The present paper is concerned with the catalytic acylation of toluene and *p*-xylene by different carboxylic acids

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