Reactions of Ketene Acetals. 8.[1] Simple Syntheses of the Methyl Ester–Ethers of the Anthraquinones Endocrocin, Ptilometric Acid, and Clavorubin

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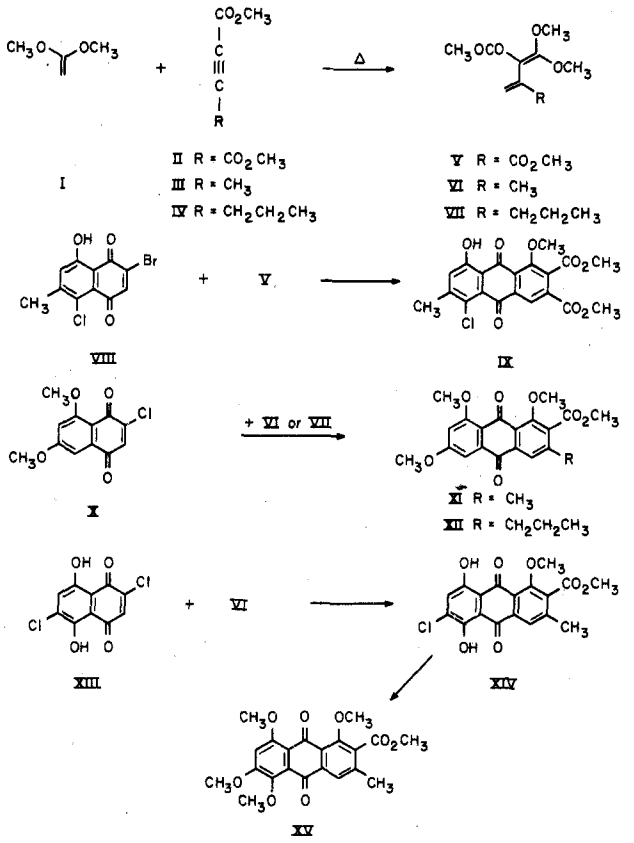
Appropriately substituted 1,1-dimethoxybutadienes (vinylketene acetals) obtained from ketene acetals and alkynoic esters were condensed with 2-chloro-6,8-dimethoxynaphthoquinone and gave directly tri-*O*-methylendocrocin methyl ester and methyl tri-*O*-methylptilometrate. An analogous reaction using 2,6-dichloronaphtazarin followed by substitution of the remaining chlorine by methoxide produced tetra-*O*-methylclavorubin methyl ester.

Ketene acetals have recently been used in order to simplify the preparation[2] of some naturally occurring anthraquinones or to elaborate some first total syntheses in this field.[1] Unsubstituted ketene acetals thus have given convenient syntheses of catenarin, helminthosporin, emodin, and indirectly of (±)-nalgiovensin (±)-isorhodoptilometrin, and (±)-rhodoptilometrin, whereas a simple conjugated reagent, isopropenylketene acetal, has been applied in the case of chrysophanol. Difficultly accessible substitution patterns as shown by the title compounds could in principle be obtained regiospecifically by the use of dienes analogous to those prepared by Brannock et al.[3]

It has been shown[3] that the reactions of ketene acetals with dimethyl acetylenedicarboxylate or methyl propiolate involved cycloadditions followed by electrocyclic processes since they eventually led to the formation of substituted 1,1-dialkoxybutadienes. The reactivity of such compounds toward 2-halonaphthoquinones was first tested using 2,3-dicarbomethoxy-1,1-dimethoxy-1,3-butadiene (V) obtained in a 47% yield from ketene dimethyl acetal (I) and dimethyl acetylenedicarboxylate (II). In spite of the presence of bulky electron-attracting groups in the diene, the latter proved to be quite reactive and a cycloaddition involving 2-bromo-5-chloro-8-hydroxy-6-methylnaphthaquinone (VIII) was complete in 1 h at 130 °C. Examination of the NMR spectrum of the crude reaction product revealed the presence of the expected anthraquinone and of another compound, probably the adduct, as indicated by aliphatic methoxyl signals at δ 3.21 and 3.29. A complete conversion to the desired product IX required an additional 3 h of heating at the same temperature.

The widely distributed metabolite endocrocin and the crinoid pigment ptilometric acid or their derivatives have until now only been synthesized by tedious means involving a large number of steps.[4-7] Attempts to prepare the appropriate dienes VI and VII from methyl tetrolate and methyl hex-2-ynoate according to the method used[3] for analogous products were unsuccessful. The reagents were, however, obtained in 35 and 28% yields, respectively, by prolonged heating (20–22 h) without solvent and at higher temperatures (145–160 °C) when large amounts (35–40%) of the unreacted esters could be recovered. By condensing these dienes with 2-chloro-6,8-dimethoxynaphthaquinone (X), which has only recently become available,[8] at 150–160 °C for 2–3 h, the permethylated derivatives of endocrocin and ptilometric acid were obtained in yields of 48 and 56%, respectively.

The minor ergot pigment clavorubin had previously been prepared by the manganese dioxide oxidation of endocrocin but only in low yield.[9] The most convenient starting material for the preparation of the completely methylated derivative of this quinone is undoubtedly 2,6-dichloronaphthazarin[10,11] (XIII). Condensation of this quinone with the diene VI as



before followed by pyrolysis at 150 °C for 1 h gave an excellent yield (87%) of the expected product XIV, thus confirming the previously observed favorable effect of peri-hydroxyl groups. The substitution of the remaining chlorine by methoxide could not be carried out in the usual manner[12,13] (CH_3ONa–CH_3OH) as the disodium salt of the substrate seems to be completely insoluble under these conditions, It could, however, be efficiently accomplished (75% after methylation) in a mixture of methanol and dimethylformamide in the presence of copper(I) iodide according to a recently published procedure.[14] Partial cleavage of the ethers is observed giving products strongly adsorbed during chromatography. The crude material was therefore methylated before purification. The resulting derivative XV has not been described earlier and an authentic sample of clavorubin could not be obtained. However, the general resemblance of the spectra of the three title compounds, the presence in the NMR spectrum of quinone XV of very characteristic signals corresponding to the protons in positions 4 and 7, and the fact that no trace of nonregiospecific products has ever been detected in this use

of ketene acetals leave very little doubt as to the precise structure of the synthetic substance.

Experimental Section

All melting points were taken for samples in capillary tubes with a Thomas-Hoover apparatus (calibrated thermometer). The ir and uv spectra were determined on Beckman Model IR-12 and Model DK-1A spectrophotometers, respectively. The NMR spectra were recorded on Varian A-60 and Bruker HX-90 spectrometers (tetramethylsilane as internal standard). Woelm silica gel, activity III, was used throughout for dry column chromatography.

2,3-Dicarbomethoxy-1,1-dimethoxy-1,3-butadiene (V). To a solution of dimethyl acetylenedicarboxylate (II, 9.50 g, 0.0668 mol) in dry acetonitrile (8 ml) was added dropwise (10 min) ketene dimethyl acetal (I,[15] 5.90 g, 0.0669 mol). The reaction mixture was stirred at room temperature (1 h), then refluxed (2 h) and evaporated. The residue was distilled under vacuum and gave the diene V (7.30 g, 48%): bp 104–106 °C (0.3 mm); n^{25}D 1.4838; ν_{max} (film) 1725 (ester) and 1600 cm^{-1} (broad, diene); δ (90 MHz, $CDCl_3$) 3.60, 3.66, 3.68 and 3.93 (4 × 3 H, 4 s, 1,1-OCH_3 and 2,3-CO_2CH_3), 5.35 and 6.26 (2 × 1 H, 2 d, J = 1.5 Hz, 4-H_2); m/e 230 (M^+). Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.08; H, 6.24.

2-Carbomethoxy-1,1-dimethoxy-3-methyl-1,3-butadiene (VI). A mixture of methyl tetrolate (III, 20.0 g, 0.204 mol) and ketene dimethyl acetal (I, 18.0 g, 0.204 mol) was heated in a sealed tube at 145 °C for 20 h and fractionated under vacuum, and gave unchanged methyl tetrolate (7.9 g, 38%), bp 50–60 °C (15 mm), and the diene VI (13.5 g, 35%): bp 106–112 °C (15 mm); n^{24}D 1.4774; ν_{max} (film) 1710 (ester), 1640 and 1601 cm^{-1} (diene); δ (60 MHz, neat) 1.83 (3 H, m, 3-CH_3), 3.60, 3.64, and 3.65 (3 × 3 H, 3 s, 1,1-OCH_3 and 2-CO_2CH_3), 4.75 and 4.97 (2 × 1 H, 2 m, 4-H_2). Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.97; H, 7.64.

Methyl Hex-2-ynoate (IV). This compound was prepared from butanoyl chloride (125.6 g, 1.18 mol) and carbomethoxymethylenetriphenylphosphorane (404.8 g, 1.21 mol) according to the method described for the ethyl ester.[16] The intermediate 1-carbomethoxy-2-oxopentylidenetriphenylphosphorane (268 g) was pyrolyzed in 50-g portions (230 °C, 10 mm) and gave methyl hex-2-ynoate (IV, 45.0 g, 59%): bp 76–80 °C (25 mm) [lit.[17] bp 80–82 °C (23 mm)]; n^{20}D 1.4409; ν_{max} (film) 2241 (triple bond) and 1715 cm^{-1} (ester); δ (90 MHz, $CDCl_3$) 1.00 (3 H, t, J = 7.0 Hz, 6-H_3), 1.61 (2 H, sextuplet, J = 7.0 Hz, 5-H_2), 2.30 (2 H, t, J = 7.0 Hz, 4-H_2), 3.70 (3 H, s, 1-CO_2CH_3); m/e 216 (M^+). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.61; H, 7.99.

2-Carbomethoxy-1,1-dimethoxy-3-propyl-1,3-butadiene (VII). A mixture of methyl hex-2-ynoate (IV, 25.2 g, 0.200 mol) and ketene dimethyl acetal (I, 17.6 g, 0.200 mol) was heated in a sealed tube at 155–160 °C for 22 h and distilled under vacuum and gave unreacted methyl hex-2-ynoate (9.7 g, 39%), bp 76–78 °C (20 mm), and the diene VII (11.9 g, 28%): bp 70–72 °C (0.5 mm); n^{24}D 1.4730; ν_{max} (film) 1707 (ester) and 1607 cm^{-1} (diene); δ (60 MHz, neat) 0.88 (3 H, t, J = 7.0 Hz, 3′-H_3), 1.40 (2 H, m, 2′-H_2), 2.14 (2 H, m, 1′-H_2), 3.55 and 3.59 (2 × 3 H, 2 s, 1,1-OCH_3), 3.74 (3 H, s, 2-CO_2CH_3), 4.75 and 4.95 (2 H, 2 m, 4-H_2). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.05; H, 8.84.

4-Chloro-6,7-dicarbomethoxy-1-hydroxy-8-methoxy-3-methylanthraquinone (IX). A mixture of 2-bromo-5-chloro-8-hydroxy-6-methylnaphthoquinone[2] (VIII, 600 mg, 1.99 mmol) and 2,3-dicarbomethoxy-1,1-dimethoxy-1,3-butadiene (V, 920 mg, 3.99 mmol) in dry benzene (1 ml) was refluxed until it become homogeneous (10 min) and then evaporated. The residue was kept at 130 °C for 4 h, cooled, and chromatographed on silica gel (60 g) (dry column, benzene–ethyl acetate, 19:1) and gave the anthraquinone IX (743 mg, 89%), mp 183.5–184.0 °C (chloroform–methanol). An analytical sample was recrystallized four times from methanol: mp 187.5–188.0 °C; λ_{max} (ethanol) 247, 282 (sh), 345, 420 nm (log ϵ 4.45, 3.96, 3.55, 3.84); ν_{max} (KBr) 1735 (ester), 1680 (carbonyl), 1640 (chelated carbonyl), 1595 cm^{-1} (aryl); δ (90 MHz, $CDCl_3$) 2.50 (3 H, s, 3-CH_3), 3.98, 4.00, and 4.01 (3 × 3 H, 3 s, 8-OCH_3 and 6,7-CO_2CH_3), 7.19 broad (1 H, s, 2-H), 8.63 (1 H, s, 5-H), and 11.90 (1 H, s, 1-OH); m/e 418/420 (M^+). Anal. Calcd for $C_{20}H_{15}ClO_8$: C, 57.35; H, 3.61; Cl, 8.46. Found: C, 57.23; H, 3.66; Cl, 8.40.

2-Carbomethoxy-1,6,8-trimethoxy-3-methylanthraquinone (Tri-*O*-methylendocrocin Methyl Ester) (XI). To a suspension of 2-chloro-6,8-dimethoxynaphthoquinone,[8] mp 209.0–209.5 °C (600 mg, 2.37 mmol), in dry benzene (6 ml) was added 2-carbomethoxy-1,1-dimethoxy-3-methyl-1,3-butadiene (VI, 666 mg, 3.58 mmol). The reaction mixture was then refluxed for 2 h, evaporated, heated at 150–155 °C for 2 h, cooled, and chromatographed on silica gel (80 g) (dry column, chloroform–ethyl acetate 9:1), and gave the anthraquinone XI (423 mg, 48%): mp 227–228 °C (benzene) (lit.[4,18] mp 225–226 °C); λ_{max} (ethanol) 227, 241, 279, 343, 395 nm (log ϵ 4.40, 4.33, 4.44, 3.63, 3.75); ν_{max} (KBr) 1729 (ester), 1662 (carbonyl), 1596, 1570, 1447, 1390, 1321, 1244 cm^{-1}; δ (90 MHz, $CDCl_3$) 2.40 broad (3 H, s, 3-CH_3), 3.95–3.97 (4 × 3 H, 4 s, 1,6,8-OCH_3 and 2-CO_2CH_3), 6.79 (1 H, d, J = 2.5 Hz, 7-H), 7.35 (1 H, d, J = 2.5 Hz, 5-H), and 7.87 broad (1 H, s, 4-H); m/e 370 (M^+). Anal. Calcd for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90. Found: C, 64.70; H, 4.88. (An authentic sample of this compound could not be obtained but the NMR spectrum in particular is in excellent agreement with that published by Venkataraman.[19])

2-Carbomethoxy-1,6,8-trimethoxy-3-propylanthraquinone (Methyl Tri-*O*-methylptilometrate) (XII). In an analogous reaction, a mixture of the naphthoquinone X (600 mg, 2.37 mmol), 2-carbomethoxy-1,1-dimethoxy-3-propyl-1,3-butadiene (VII, 1.520 g, 7.09 mmol), and benzene (2 ml) was refluxed for 30 min, evaporated, and heated at 160 °C for 3 h. Methanol (4 ml) was added to the cooled residue and the resulting suspension was filtered after 12 h giving the anthraquinone XII (454 mg), mp 149–150 °C. Chromatography of the mother liquor on silica gel (40 g) (dry column, chloroform–ethyl acetate, 9:1) provided another portion (78 mg) of the same substance, mp 150–151 °C (methanol) (total yield 56%). An analytical sample was recrystallized three times from the same solvent: mp 154.5–155.0 °C (lit.[20] 155–156,[6] 148.5–151.0 °C); λ_{max} (ethanol) 227, 243, 281, 345, 390 nm (log ϵ 4.38, 4.32, 4.41, 3.63, 3.73); ν_{max} (KBr) 1718 (ester), 1667 (carbonyl), and 1598 cm^{-1} (aryl); δ (90 MHz, $CDCl_3$) 0.96 (3 H, t, J = 7.0 Hz, 3′-H_3), 1.71 (2 H, m, 2′-H_2), 2.62 (2 H, t, J = 7.5 Hz, 1′-H_2), 3.93, 3.95, and 3.96 (3 H, 6 H and 3 H, 3 s, 1,6,8-OCH_3 and 2-CO_2CH_3), 6.75 (1 H, d, J = 2.5 Hz, 7-H), 7.32 (1 H, d, J = 2.5 Hz, 5-H) 7.89 broad (1 H, s, 4-H); m/e 398 (M^+). Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 66.08; H, 5.52. The synthetic substance was identical (mixture melting point, TLC in four solvent systems, and ir spectra) with an authentic sample kindly provided by Professor M. D. Sutherland.

2-Carbomethoxy-6-chloro-5,8-dihydroxy-1-methoxy-3-methylanthraquinone (XIV). A suspension of 2,6-dichloronaphthazarin (XIII, 1.000 g, 3.86 mmol) and the diene VI (1.080 g, 5.80 mmol) in dry benzene (3 ml) was refluxed until it becomes homogeneous. The mixture was then evaporated; the residue was heated at 150 °C for 1 h, refluxed in methanol (10 ml), cooled, and filtered and gave the anthraquinone XIV (1.263 g, 87%), mp 184–186 °C. An analytical sample was twice recrystallized from 1,2-dichloroethane: mp 187–188 °C; λ_{max} (ethanol) 234, 257, 294, 350, 470 nm (log ϵ 4.36, 4.32, 3.87, 3.31, 3.88); ν_{max} (KBr) 1718 (ester), 1618 (chelated carbonyl), and 1573 cm^{-1} (aryl); δ (90 MHz, $CDCl_3$) 2.45 (3 H, s, 3-CH_3), 3.97 and 4.00 (2 × 3 H, 2 s, 1-OCH_3 and 2-CO_2CH_3), 7.40 (1 H, s, 7-H), 8.03 broad (1 H, s, 4-H), 13.24 and 13.45 (2 × 1 H, 2 s, 5,8-OH); m/e 376/378 (M^+). Anal. Calcd for $C_{18}H_{13}ClO_7$: C, 57.38; H, 3.48; Cl, 9.41. Found: C, 57.53; H, 3.29, Cl, 9.45.

2-Carbomethoxy-1,5,6,8-tetramethoxy-3-methylanthraquinone (Tetra-*O*-methylclavorubin Methyl Ester) (XV). To a solution of sodium (2.00 g, 0.0869 mol) in absolute methanol (20 ml) was added dimethylformamide (20 ml), copper(I) iodide (200 mg), and the foregoing quinizarin XIV (200 mg, 0.531 mmol). The mixture was refluxed for 2 h, poured on ice (200 g), acidified with dilute hydrochloric acid, and filtered. The residue was methylated in the usual way with dimethyl sulfate (500 mg) and potassium carbonate (1.23 g) in refluxing acetone (20 ml, 10 h). The crude product was chromatographed on silica gel (60 g) (dry column, chloroform–ethyl acetate, 9:1) and gave the anthraquinone XV (160 mg, 75%): mp 191.5–192.0 °C (methanol); λ_{max} (ethanol) 230, 248, 282, 410 nm (log ϵ 4.37, 4.34, 4.17, 3.75); ν_{max} (KBr) 1722 (ester), 1666 (carbonyl), and 1588 cm^{-1} (aryl); δ (90 MHz, $CDCl_3$) 2.38 (3 H, s, 3-CH_3), 3.94, 3.95, and 3.98 (3 H, 3 H, and 9 H, 3 s, 1,5,6,8-OCH_3 and 2-CO_2CH_3), 6.81 (1 H, s, 7-H), and 7.75 (1 H, s, 4-H); m/e 400 (M^+). Anal. Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 62.83; H, 5.04.

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Registry No.—I, 922-69-0; II, 762-42-5; III, 23326-27-4; IV, 18937-79-6; V, 59696-63-8; VI, 59696-64-9; VII, 59696-65-0; VIII, 52431-63-7; IX, 59711-76-1; X, 57165-99-8; XI, 59696-66-1; XII, 15939-13-6; XIII, 13719-93-2; XIV, 59696-67-2; XV, 59696-68-3; 1-carbomethoxy-2-oxopentyldenetriphenylphosphorane, 59696-69-4.

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Nickel-Promoted Isomerizations of Alkenes Bearing Polar Functional Groups

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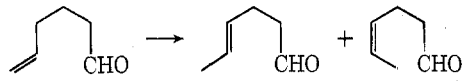
A catalyst derived from ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (1) and hydrogen chloride has been found to isomerize a variety of alkenes bearing polar functional groups. Treatment of 5-hexenal and ethyl 4-pentenoate with the catalyst in hexane or toluene solution at 25 °C afforded essentially quantitative yields of the geometric isomer mixtures of 4-hexenal and of ethyl 3-pentenoate, respectively. High-yield catalytic conversions of 5-chloro-1-pentene and of 4-penten-1-ol to 5-chloro-2-pentene and 3-penten-1-ol, respectively, were also achieved. The configurationally specific conversion of allyl phenyl ether to phenyl *cis*-propenyl ether was accomplished in high yield. A number of allylic alcohols were isomerized to saturated carbonyl compounds by 1 and HCl. Allyl alcohol, 1-hexen-3-ol, 2-cyclohexen-1-ol, 2-methyl-2-propen-1-ol, 3-penten-2-ol, 2-buten-1-ol, and 1,4-pentadien-3-ol were converted to propanal, 3-hexanone, cyclohexanone, 2-methylpropanal, 2-pentanone, 1-butanal, and penten-3-one, respectively. The ethylenebis(tri-*o*-tolyl phosphite)nickel(0)–hydrogen chloride system catalyzed the skeletal rearrangement of *cis*-1,4-hexadiene to *trans*-2-methyl-1,3-pentadiene in 1-butanol and ethyl hexanoate solvents. This transformation was accompanied by the formation of *cis,cis*- and *trans,cis*-2,4-hexadienes. Treatment of 2,5-hexadien-1-ol with the catalyst system in hexane solvent afforded *trans*-4-methyl-2,4-pentadien-1-ol as major product along with lesser amounts of 5-hexenal. When 2,5-hexadien-1-ol was treated with the catalyst in ethylene-saturated hexane, *trans*-4-methyl-2,4-pentadien-1-ol, 5-hexenal, *cis*-4-hexenal, and *cis,cis*-2,4-hexadien-1-ol were formed.

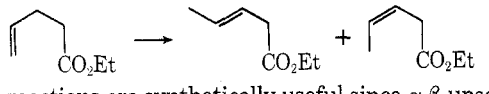
Soluble nickel-based catalysts can promote double bond positional isomerizations of simple alkenes[1] and polyenes[1c,2] as well as skeletal isomerizations of certain dienes.[2a,3] While the reactions of afunctional alkenes have been studied quite extensively, the applicability of the catalysts to isomerizations of alkenes bearing polar functional groups has not received much attention. In some cases, the natures of the catalyst precursors have been responsible for the limited scope of inquiry. For instance, the first catalysts which were found to cleave carbon–carbon σ bonds in dienes to afford rearranged products were derived from in situ reactions of nickel(II) complexes with alkylaluminum compounds.[2a,3] The aluminum cocatalysts react with most polar functional groups. Our findings that catalysts derived from ethylenebis(triarylphosphine)nickel(0) complexes and hydrogen halides accomplish both the 1,4-pentadiene to isoprene type rearrangement and alkene double bond migration reactions[3-5] offered the probability that isomerizations of functionally substituted alkenes could be achieved. The compatibility of this type of catalyst system with polar molecules was demonstrated by the successful isomerization of *cis*-1,4-hexadiene by ethylenebis(tri-*o*-tolyl phosphite)nickel(0) (1) and hydrogen chloride in 1-butanol solvent. During 5 min at room temperature, *trans*-2-methyl-1,3-pentadiene and *trans,cis*- and *cis,cis*-2,4-hexadienes were afforded in 26, 6, and 26% yields, respectively, at 78% conversion of the 1,4-diene to products when a 12:1:0.8 diene:Ni:HCl molar ratio was employed. Comparable results were obtained when ethyl hexanoate solvent was used. These results induced our discovery that a variety of alkenes bearing polar functional groups could be isomerized in high yield by the 1/HCl catalyst system.

Treatment of 5-hexenal with 1 and HCl in toluene or hexane solvents afforded essentially quantitative yields of *trans*- and *cis*-4-hexenal at 100% conversion when aldehyde:Ni ratios as high as 50:1 were employed, eq 1. In a like manner, ethyl 4-



(1)

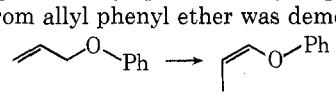
pentenoate was converted to a mixture of *trans*- and *cis*-ethyl 3-pentenoate in quantitative yield at 83% conversion, eq 2.



(2)

These reactions are synthetically useful since α,β-unsaturated carbonyl compounds are not generated, but the double bond migration can be controlled to produce nonconjugated products. High-yield catalytic isomerizations of 5-chloro-1-pentene and of 4-penten-1-ol were also achieved.

The configurationally specific catalytic generation of an enol ether from allyl phenyl ether was demonstrated, eq 3.



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