Ruthenium(II) Catalyzed Rearrangement of Diallyl Ethers. A Synthesis of γ,δ-Unsaturated Aldehydes and Ketones

James M. Reuter and Robert G. Salomon*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received April 4, 1977

Synthesis and selective tris(triphenylphosphine)ruthenium(II) dichloride catalyzed rearrangement of unsymmetrical diallyl ethers to γ,δ-unsaturated aldehydes and ketones are reported. Presumably ruthenium regiospecifically promotes olefin isomerization to allyl vinyl ethers which undergo Claisen rearrangement. Isomerization of monosubstituted olefins occurs more rapidly than isomerization of vicinally disubstituted olefins. Geminally disubstituted or trisubstituted olefins do not isomerize readily. Remarkably, an allyl ether rearranges six times more readily than an α-methylallyl ether.

The aliphatic Claisen rearrangement, first observed in enol allyl ethers in 1912,[1] was not recognized[2] as a generally useful and important reaction until recently.[3] The rearrangement was extended to simple allyl vinyl ethers 26-years later.[4] It has been studied mechanistically by a number of investigators.[5] The high stereoselectivity for the formation of (*E*)-di- and trisubstituted olefins upon Claisen rearrangement of vinyl ethers of secondary allylic alcohols has recently found many applications in organic synthesis.[6] This stereoselectivity extends to the creation of asymmetric centers in high optical yield.[7,8] The Claisen rearrangement is now recognized as an important general, stereoselective method for olefin synthesis. The above types of Claisen rearrangements as well as some more recent variants have found extensive application in the synthesis of natural products.[9]

The allyl vinyl ether substrates for Claisen synthesis of γ,δ-unsaturated aldehydes or ketones are generally prepared by acid-catalyzed decomposition of diallyl acetals[4,10] or transvinylation.[11,12] Schemes involving allyl ethers of halohydrins,[4,13] vinylation[14] of α-halo ethers, or Wittig olefination[15] have also been employed. Allyl enol ethers of acetoacetic esters[1] and zinc enolates of allyl or propargyl esters[16] are also useful. We now report that selective rearrangement of diallyl ethers catalyzed by tris(triphenylphosphine)ruthenium(II) dichloride is a valuable new route for the synthesis of γ,δ-unsaturated aldehydes and ketones. Preliminary rearrangement to allyl vinyl ethers followed by Claisen rearrangement presumably is involved.

Results

Preparation of Diallyl Ethers. Unsymmetrical diallyl ethers **2** are readily available in high yields by *O*-alkylation of allyl alcohols **1** with allyl halides (Table I).

Ruthenium Catalyzed Rearrangement of Diallyl Ethers. The diallyl ethers were heated at 200 °C in the presence of 0.1 mol % tris(triphenylphosphine)ruthenium dichloride in sealed Pyrex tubes for 1–4 h. Simple short-path distillation of the reaction product mixture gave good to excellent yields of γ,δ-unsaturated carbonyl compounds **3** which were often better than 90% pure according to GLC and ^{1}H NMR analysis. In principle, two different isomeric γ,δ-unsaturated carbonyl compounds could be produced from each unsymmetrical diallyl ether. Generally, however, the isomer shown in Table II was the only carbonyl product obtained.

2d → **3d** + **2d′** + HO

The structures assigned to the products **3a–i** are supported by their ^{1}H NMR spectra (see below and Experimental Section). The rearrangement of **2d** to **3d** was accompanied by the formation of the ether **2d′** (13%) and methylallyl alcohol (10%). The ether **2d′** was identified by ^{1}H NMR and GLC comparison with an authentic sample prepared by *O*-alkylation of Δ^3-cyclopentenol with methallyl chloride.

3c **3e** **3f**

The ^{1}H NMR spectra of the product aldehydes **3c, 3e,** and **3f** suggested the presence of two diastereomers. Two doublets with equal coupling constants were observed in each case for the methyl group α to the carbonyl. The diastereomers of **3e** were separable by GLC.

2i → **3i** + **3i′** (6:1)

Rearrangement of **2i** gave predominantly **3i.** The *E* configuration of the C–C π bond in **3i** is assumed due to the known stereoselectivity of such Claisen rearrangements.[6] The aldehyde was readily separated quantitatively from the reaction product mixture as the water-soluble sodium bisulfite addition product. The water insoluble product mixture yielded the ketone **3i′** (9%) and starting material **2i** (30%). The ketone **3i′** was identified by ^{1}H NMR and GLC comparison with an authentic sample.[20] The aldehyde **3i** was recovered from the aqueous phase after treatment with saturated sodium bicarbonate. Ozonolysis of the major product **3i** followed by oxidation gave methylsuccinic acid (**4i**) exclusively.

3i → (1. O_3; 2. HCOOH, H_2O_2) → **4i**

Table I. Synthesis of Unsymmetrical Diallyl Ethers

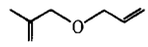
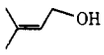
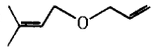
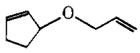
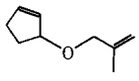
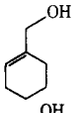
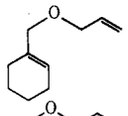
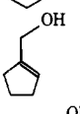
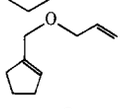
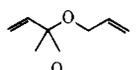
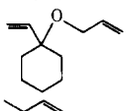
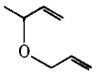
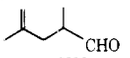
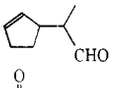
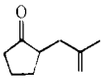
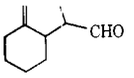
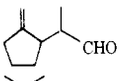
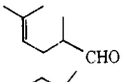
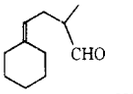
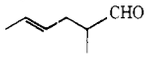
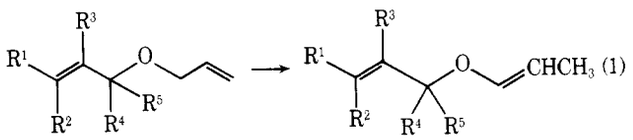
Alcohol	Registry no.	Halide	Registry no.	Ether	Yield, %	Registry no.
1a 	513-42-8		106-95-6	2a 	88	14289-96-4
1b 	556-82-1			2b 	91	63163-49-5
1c 	107-18-6		96-40-2	2c 	80	63163-50-8
1d 	3212-60-0		563-47-3	2d 	89	63163-51-9
1e 	4845-04-9			2e 	79	63163-52-0
1f 	1120-80-5			2f 	81	63163-53-1
1g 	115-18-4			2g 	92	63163-54-2
1h 	1940-19-8			2h 	86	63163-55-3
1i 	598-32-3			2i 	85	37027-64-8

Table II. Ruthenium Catalyzed Rearrangement of Unsymmetrical Diallyl Ethers

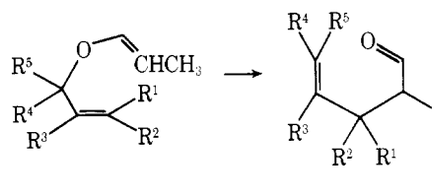
Diallyl ether	Product	Reaction time, h	Isolated yield, %	GC purity, %
2a	3a 	1	92	89[a]
2b	3b 	1	90	99
2c	3c 	1.5	71	100
2d	3d 	3	56	70[b]
2e	3e 	1.5		95[c]
2f	3f 	1.5	84	93
2g	3g 	4	80	92
2h	3h 	2	78	83[d]
2i	3i 	4	55[e]	100

[a] Distilled reaction product mixture contained 8% starting ether **2a**. [b] Also isolated: Δ^3-cyclopentenyl methylallyl ether and methylallyl alcohol, see below. [c] Diastereomers separable on 10 ft × ¼ in. 10% Carbowax 20M on 60/80 Chromosorb W. [d] Distilled reaction product mixture contained 7% starting ether **2h**. [e] Isolation of **3i** was affected by sodium bisulfite extraction—see Experimental Section.

Transition metal catalyzed conversion of monoallyl ethers into vinyl ethers is known.[17] Platinum hydrides promote *cleavage* of diallyl ethers to give aldehydes and π-allylplatinum(II) complexes rather than rearrangement.[18] We now find that tris(triphenylphosphine)ruthenium(II) dichloride catalyzes *rearrangement* of diallyl ethers to give γ,δ-unsaturated carbonyl compounds. These ruthenium catalyzed rearrangements of diallyl ethers almost certainly involve generation (eq 1) and subsequent Claisen rearrangement (eq 2) of allyl vinyl ethers.

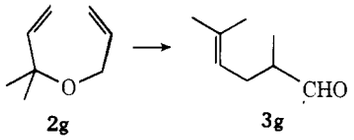


(1)

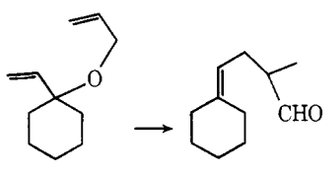


(2)

The rearrangements listed in Table II exhibit two noteworthy features. Allylic rearrangement is *highly regiospecific*. Secondly, the products **3** of the Claisen rearrangement do not undergo further ruthenium catalyzed allylic rearrangement. These features are readily understandable if it is recognized that ruthenium catalysis of allylic hydrogen migration occurs less readily for substituted olefins. The ease of olefin isomerization shows a strong sensitivity to structural factors and rates of rearrangement vary greatly with olefin structure.[19]



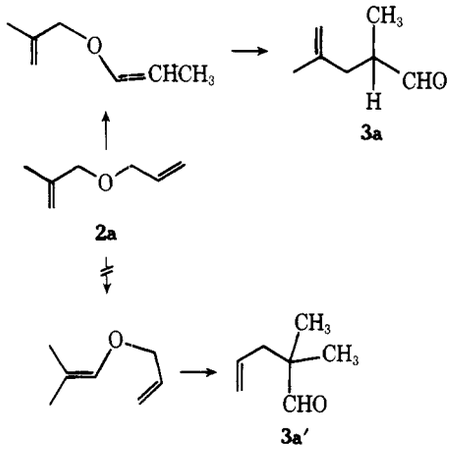
2g **3g**



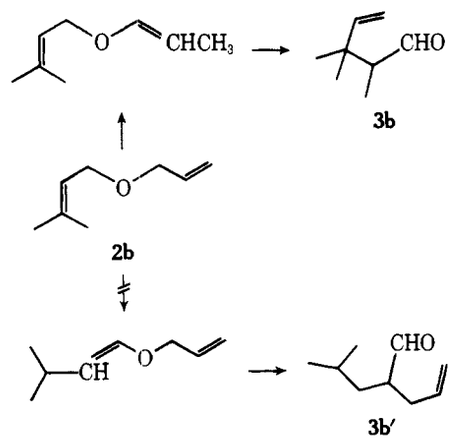
2h **3h**

Of course, for the ethers **2g** and **2h,** migration of an allylic hydrogen can occur from only one position. Thus, Claisen rearrangement of the intermediate allyl vinyl ether results in a single product **3g** or **3h.**

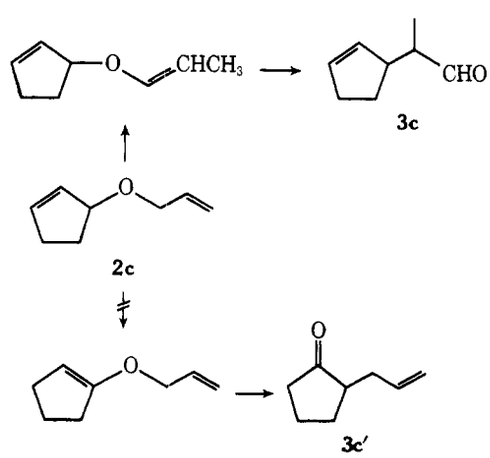
The influence of olefin substitution on the relative ease of allylic hydrogen migration may be deduced from a consider-



ation of the rearrangements observed for **2a–f** and **2i.** The ether **2a** contains a geminally disubstituted olefin and a monosubstituted olefin. Only a single Claisen product is observed. Only the monosubstituted π bond undergoes ruthenium catalyzed allylic rearrangement. An ^1H NMR spectrum of the crude reaction product mixture shows the complete disappearance of the CH vinylic methine proton of **2a** and the absence of a six-hydrogen singlet which is expected for the *gem*-dimethyl substituents α to the carbonyl in **3a'.**

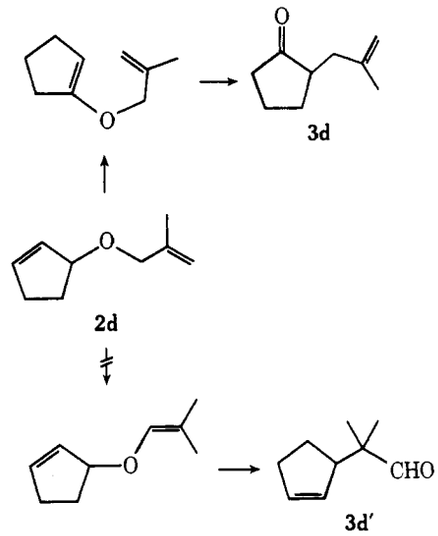


Ether **2b** contains a trisubstituted olefin and a monosubstituted olefin. Again, only the monosubstituted π bond undergoes ruthenium catalyzed allylic rearrangement, and only a single Claisen product is observed. Inspection of the ^1H

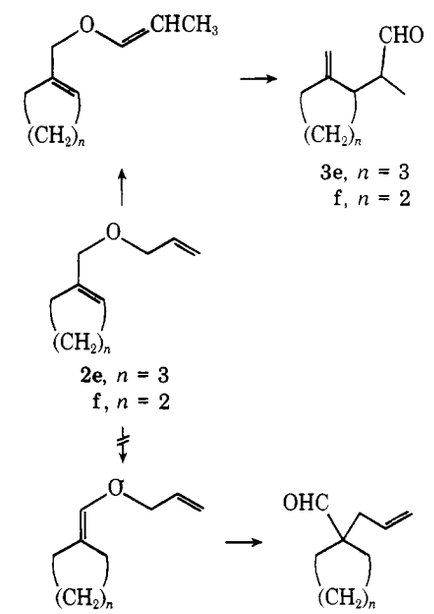


NMR spectrum of the crude reaction mixture shows a six-proton singlet which is accounted for by quaternary *gem*-dimethyl substituents in **3b.** The alternative product **3b'** would show a six-hydrogen doublet due to its *gem*-dimethyl substituents. Such a doublet is not observed.

In the case of **2c** the monosubstituted olefin isomerizes in preference to the vicinally disubstituted olefin. An ^1H NMR spectrum shows a one-proton doublet assignable to the aldehydic hydrogen corresponding to the structure **3c.** Also, a single downfield tertiary ring proton is observed, which is due to the allylic methine in **3c,** and two diastereomeric methyl doublets appear at δ 1.04 and 1.07 (J = 7 Hz). Interestingly in **2d,** in contrast with **2c,** only the vicinally disubstituted π bond migrates and therefore no aldehyde **3d'** is produced.

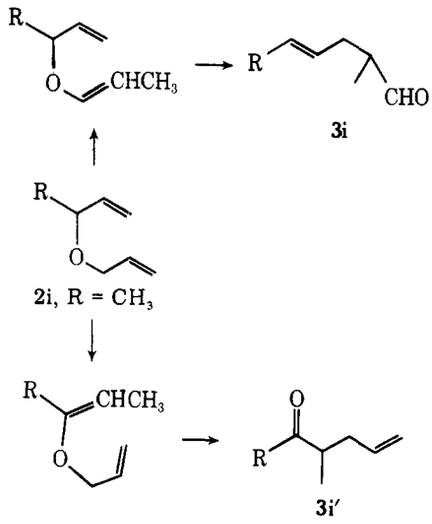


Not surprisingly, olefin isomerization followed by Claisen rearrangement in **2e** and **2f** results in a single rearrangement product. A ^1H NMR spectrum shows two diastereomeric al-



dehydic proton doublets for both the crude and GC isolated products from **2e.** Also, as for **3c,** both **3e** and **3f** show diastereomeric methyl groups.

The most remarkable example of selectivity in ruthenium catalyzed rearrangement of diallyl ethers occurs in **2i.** The products **3i** and **3i'** are formed in the ratio of 6:1 where R = CH_3. This unexpected result suggests that even *allylically substituted monoolefins direct the specificity of ruthenium catalyzed allylic hydrogen isomerization.* This extraordinary



reaction should be general and highly regiospecific for any derivative of **2i** in which R has steric requirements equal to or greater than a methyl group.

Conclusion

Unsymmetrical diallyl ethers give γ,δ-unsaturated ketones or aldehydes upon heating in the presence of tris(triphenylphosphine)ruthenium dichloride. Presumed intermediate allyl vinyl ethers produced by an initial ruthenium catalyzed 1,3-hydrogen shift give the observed products by Claisen rearrangement. Rearrangement of unsymmetrical diallyl ethers is predictably regiospecific, since 1,3-hydrogen migration occurs readily only with mono and vicinally disubstituted olefins. Furthermore, the rates of rearrangement vary considerably with olefin substitution. Isomerization of monosubstituted olefins occurs more rapidly than isomerization of vicinally disubstituted olefins. Even a mere allylic methyl substituent markedly retards 1,3-hydrogen migration.

Experimental Section

General. All vessels were flame dried and reactions, whenever possible, were carried out under an atmosphere of nitrogen. Solvents were freshly distilled. All GC work was performed with a Varian Model 90-P using a 6 ft SE 30 15% on Chromosorb W 60/80; NMR spectra recorded with a Varian A60A or HA-100 with Fourier transform using CCl_4 and 1% Me_4Si as solvent. All sealed tube reactions were done behind a safety shield.

Ether Synthesis A. Allyl Methylcyclopentenyl Ether (2f). NaH (2.0 g, 46 mmol, 57% oil dispersion) in a 100-mL three-necked flask equipped with reflux condenser, mechanical stirrer, and addition funnel was washed with pentane (two 10-mL portions). THF (75 mL) was then added followed by the portionwise addition of cyclopentene-1-carbinol (3.0 g, 30 mmol), and the resulting mixture was stirred under reflux for 2 h. Then while the mixture was still warm, HMPA (15 mL) was added followed by allyl bromide (5.5 g, 45 mmol) at such a rate as to maintain a gentle reflux. Upon addition, the mixture was again boiled under reflux for 2 h. The reaction mixture was allowed to cool to room temperature, quenched with 10% aqueous HCl (25 mL), and extracted with pentane (two 50-mL portions). The combined organic fractions were washed with 10% aqueous HCl, saturated $NaHCO_3$, H_2O, and saturated NaCl, and dried ($MgSO_4$). Solvent removal with rotary evaporation and distillation of the crude product yielded the title ether, 3.4 g (81%), bp 62 °C (10 mm).

Method B. Allyl Δ²-Cyclopentenyl Ether (2c). Δ²-Cyclopentenyl chloride (102 g, 1 mol) was added dropwise with vigorous mechanical stirring to a suspension of $NaHCO_3$ (170 g, 2 mol) in allyl alcohol (464 g, 8 mol) at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 15 h. Inorganic salts were removed by suction filtration and the organic solution was distilled. Excess allyl alcohol was recovered and then the product was obtained, 98 g (80%), bp 131–132 °C.

Yield Optimization for Claisen Rearrangement. Maximum yields for the ruthenium catalyzed Claisen rearrangements were determined as follows: six to ten half-filled sealed Pyrex tubes were prepared, each containing 150 μL of a solution obtained from 1.0–1.5 g of the starting ether and 0.1 mol % tris(triphenylphosphine)ruthenium dichloride. The catalyst was first dissolved in the neat ether by gentle heating and shaking. The sealed tubes were placed in a 200 °C oil bath. One tube was removed every 0.5 h and the contents were analyzed by ^1H NMR.

Preparative Claisen Rearrangements. In general the starting ether (5 g) and tris(triphenylphosphine)ruthenium dichloride (0.1 mol %) were vacuum sealed in a Pyrex tube (i.d. 1.3 cm, o.d. 1.6 × 25 cm). The tubes, when sealed, were never more than half filled. The mixtures were then heated in an oil bath at 200 °C for a predetermined time, cooled to room temperature, and carefully opened. The product mixtures were vacuum transferred to remove all traces of catalyst and carefully distilled.

Separation of 2-Methylhex-4-enal (3i). The crude reaction mixture (3.4 g) was vacuum transferred to remove catalyst and shaken with sodium bisulfite (6.4 g, 0.062 mol) in water (10 mL). After several minutes of agitation the aqueous layer was extracted with ether (two 2-mL portions). The combined organic fractions were dried ($MgSO_4$) and the solvent was removed by distillation, yielding a mixture of starting material (1.0 g) and 4-methylhex-1-en-5-one (0.3 g). To the aqueous layer was cautiously added saturated $NaHCO_3$ (vigorous) until CO_2 evolution ceased. The aldehydic product was then obtained (1.9 g, 55%) by continuous ether extraction (12 h) of the aqueous mixture and removal of the solvent by careful distillation.

2-Methylsuccinic Acid.[21] 2-Methylhex-4-enal (500 mg, 4.45 mmol) in methanol (15 mL) was ozonized at −70 °C until the solution appeared slightly blue. The methanol was then removed and 98% formic acid (6 mL) and 30% hydrogen peroxide (3 mL) were added and heat was cautiously applied until a vigorous reaction began. After the reaction subsided, the mixture was boiled under reflux for 30 min. After cooling, the volatile by-products were removed with rotary evaporation and then under high vacuum to yield the title compound (510 mg, 87%, mp 115 °C). Its NMR spectrum was compared with that of an authentic sample.[22]

Allyl 2-Methylallyl Ether (2a): bp 109 °C; NMR (CCl_4) δ 1.72 (3 H, s, CH_3), 3.75–4.00 (4 H, m, CH_2OCH_2), 4.7–6.2 (5 H, m, vinyl).[23]

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.86; H, 10.40.

Allyl 3,3-Dimethylallyl Ether (2b): bp 145 °C; NMR (CCl_4) δ 1.65 (3 H, s, CH_3), 1.75 (3 H, s, CH_3), 3.87 (4 H, m, CH_2OCH_2), 4.9–6.18 (4 H, m, vinyl).[24]

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.41; H, 11.30.

Allyl Δ²-Cyclopentyl Ether (2c): bp 131–132 °C; NMR (CCl_4) δ 1.48–2.73 (4 H, m, ring CH_2's), 3.91 (2 H, d, J = 5 Hz, CH_2), 4.53 (1 H, br d, J = 5 Hz, CH), 4.90–5.36 (2 H, m, vinyl CH_2), 5.63–6.25 (3 H, m, vinyl CH, ring CH=CH).[25]

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 76.93; H, 9.60.

Δ²-Cyclopentenyl 2-Methylallyl Ether (2d): bp 165–167 °C; NMR (CCl_4) δ 1.71 (3 H, s, CH_3), 1.50–2.58 (4 H, m, ring CH_2's), 3.81 (2 H, s, CH_2), 4.48 (1 H, br d, J = 5 Hz, CH), 4.84 (2 H, br d, J = 6 Hz, vinyl CH_2), 5.88 (2 H, m, ring CH=CH).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.96; H, 10.54.

Allyl 1-Cyclohexenylmethyl Ether (2e): bp 54 °C (8.9 mm); NMR (CCl_4) δ 1.40–2.16 (8 H, m, ring CH_2's), 3.68–3.92 (4 H, m, CH_2OCH_2), 4.94–6.18 (4 H, m, vinyl).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.91; H, 10.82.

Allyl 1-Cyclopentenylmethyl Ether (2f): bp 62 °C (10.0 mm); NMR (CCl_4) δ 1.41–2.50 (6 H, m, ring CH_2's), 3.8–4.0 (4 H, m, CH_2OCH_2), 4.9–6.2 (4 H, m, vinyl).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.83; H, 10.24.

Allyl 1,1-Dimethylallyl Ether (2g): bp 120 °C; NMR (CCl_4) δ 1.24 (6 H, s, $2CH_3$'s), 3.78 (2 H, dt, J = 5 and 1 Hz, CH_2), 4.87–5.33 (4 H, m, 2 vinyl CH_2's), 5.50–6.18 (2 H, m, 2 vinyl CH's).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.03; H, 11.14.

Allyl 1-Vinylcyclohexyl Ether (2h): bp 47 °C (1.8 mm); NMR (CCl_4) δ 1.0–2.0 (10 H, m, ring CH_2's), 3.72 (2 H, dt, J = 5 and 1.2 Hz, CH_2), 4.84–5.39 (4 H, m, 2 vinyl CH_2's), 5.46–6.11 (2 H, m, 2 vinyl CH's).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.77; H, 10.82.

Allyl 1-Methylallyl Ether (2i): bp 96 °C; NMR (CCl_4) δ 1.23 (3 H, d, J = 6.5 Hz, CH_3), 3.62–4.12 (3 H, m, CH_2CH), 4.94–5.43 (4 H, m, vinyl CH_2's), 5.47–6.27 (2 H, m, vinyl CH's).

Anal. Calcd for $C_7H_{12}O$: C, 74.98; H, 10.78. Found: C, 74.81; H 10.30.

2,4-Dimethylpent-4-enal (3a): bp 128 °C; NMR (CCl_4) δ 1.07 (3 H, d, J = 6 Hz, CH_3), 1.73 (3 H, br s, CH_3), 1.76–2.60 (3 H, m, CH_2CH), 4.75 (2 H, m, vinyl CH_2), 9.56 (1 H, d, J = 1.8 Hz, CHO).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.05; H, 11.05.

2,3,3-Trimethylpent-4-enal (3b): bp 140 °C; NMR (CCl_4) δ 0.99 (3 H, d, J = 7 Hz, CH_3), 1.09 (6 H, s, $2CH_3$), 2.17 (1 H, qd, J = 7 and 2 Hz, CH), 4.78–5.20 (2 H, m, vinyl CH_2), 5.59–6.14 (1 H, m, vinyl CH), 9.64 (1 H, d, J = 2.5 Hz, CHO).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C,76.09; H, 11.23.

2-(Δ^2-Cyclopentenyl)propanal (3c): bp 150–155 °C; NMR (CCl_4) δ 1.04 (1 H, d, J = 7 Hz, CH_3), 1.07 (2 H, d, J = 7 Hz, CH_3), 1.50–2.54 (5 H, m, ring CH_2's), 2.98 (1 H, br s, CH), 5.5–5.9 (2 H, m, CH=CH), 9.71 (1 H, d, J = 2 Hz, CHO).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.43; H, 9.81.

2-(2-Methylallyl)cyclopentanone (3d): bp 82–84 °C (10.0 mm); NMR (CCl_4) δ 1.26–2.68 (9 H, m, ring CH_2's, ring CH, CH_2), 1.73 (3 H, s, CH_3), 4.68 (2 H, s, vinyl CH_2).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.52; H, 10.25.

2-(2-Methylenecyclohexyl)propanal (3e): NMR (CCl_4) δ, two GLC separable diasteriomers. Isomer 1: 1.00 (3 H, d, J = 7 Hz, CH_3), 1.60 (8 H, br s, ring CH_2's), 2.15–2.69 (2 H, m, CH), 4.69 (2 H, d, J = 9 Hz, vinyl CH_2), 9.52 (1 H, d, J = 4 Hz, CHO). Isomer 2: 1.07 (3 H, d, J = 7 Hz, CH_3), 1.57 (8 H, br s, ring CH_2's), 1.71–2.77 (2 H, m, CH), 4.64 (2 H, d, J = 15 Hz, vinyl CH_2), 9.58 (1 H, d, J = 2 Hz, CHO).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.15; H, 10.59.

2-(2-Methylenecyclopentyl)propanal (3f): bp 65 °C (9.0 mm); NMR (CCl_4) δ 1.06 (1.5 H, d, J = 7 Hz, CH_3), 1.02 (1.5 H, d, J = 7 Hz, CH_3), 1.34–2.97 (8 H, m), 4.68–5.07 (2 H, m, vinyl CH_2), 9.65 (1 H, m, CHO).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.21; H, 10.44.

2,5-Dimethylhex-4-enal (3g): bp 148 °C; NMR (CCl_4) δ 1.07 (3 H, d, J = 6 Hz, CH_3), 1.68 (6 H, d, J = 4.5 Hz, $2CH_3$'s), 1.96–2.44 (3 H, m, CH_2, CH), 4.91–5.25 (1 H, m, vinyl CH), 9.56 (1 H, d, J = 1.5 Hz, CHO).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.30; H, 11.27.

4-Cyclohexylidene-2-methylbutanal (3h): bp 85–90 °C (5.3 mm); NMR (CCl_4) δ 1.06 (3 H, d, J = 6 Hz, CH_3), 1.56 (6 H, m, ring CH_2's), 2.83–2.54 (7 H, m), 5.02 (1 H, br t, J = 7 Hz, vinyl CH), 9.58 (1 H, d, J = 1.2, CHO).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.19; H, 10.66.

2-Methylhex-4-enal (3i): bp 101 °C; NMR (CCl_4) δ 1.08 (3 H, d, J = 6 Hz, CH_3), 1.67 (3 H, d, J = 4 Hz, CH_3), 1.92–2.56 (3 H, m, CH, CH_2), 5.29–5.76 (2 H, m, CH=CH), 9.55 (1 H, d, J = 1 Hz, CHO).

Anal. Calcd for $C_7H_{12}O$: C, 74.98; H, 10.78. Found: C, 74.75; H, 10.56.

Δ^3-Cyclopentenyl 2-Methylallyl Ether (2d'): NMR (CCl_4) δ 1.70 (3 H, s, CH_3), 2.2–2.6 (4 H, m, ring CH_2's), 3.76 (2 H, s, CH_2), 4.09–4.21 (1 H, m, ring CH), 4.81 (2 H, d, J = 9 Hz, vinyl CH_2), 5.61 (2 H, s, CH=CH).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.12; H, 10.25.

4-Methylhex-1-en-5-one (3i'): NMR (CCl_4) δ 1.04 (3 H, d, J = 6 Hz, CH_3), 1.98 (3 H, s, CH_3), 1.88–2.65 (3 H, m, CH, CH_2), 4.63–5.05 (2 H, m, vinyl CH_2), 5.19–5.92 (1 H, m, vinyl CH).

2-Methylsuccinic Acid (4i): mp 111 °C (reported[22] mp 115°C); NMR ($CDCl_3$) δ 1.45 (3 H, d, J = 6 Hz, CH_3), 2.50–3.29 (3 H), 9.42 (2 H, s, COOH).

Acknowledgment. We thank the National Science Foundation for generous support of our investigations on homogeneous catalysis in organic synthesis.

Registry No.—2d', 63163-56-4; **3a,** 5187-72-4; **3b,** 61740-76-9; **3c** isomer I, 63163-57-5; **3c** isomer II, 63163-60-0; **3d,** 57133-53-6; **3e** isomer I, 63163-58-6; **3e** isomer II, 63163-61-1; **3f** isomer I, 63163-59-7; **3f** isomer II, 63163-62-2; **3g,** 870-17-1; **3h,** 32803-38-6; **3i,** 16134-69-3; **3i',** 2550-22-3; **4i,** 498-21-5; ruthenium, 7440-18-8.

References and Notes

(1) L. Claisen, *Ber.*, **35,** 3157 (1912).
(2) Review: D. S. Tarbell, *Org. React.*, **2,** 1 (1944).
(3) Reviews: (a) A. Jefferson and F. Scheinmann, *Q. Rev., Chem Soc.*, **22,** 391 (1968); (b) S. J. Rhoads and N. R. Raulins, *Org. React.*, **22,** 1 (1975).
(4) C. Hurd and M. Pollack, *J. Am. Chem. Soc.*, **60,** 1905 (1938).
(5) (a) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87,** 4388 (1965); (b) K. Fukui and H. Fujimoto, *Tetrahedron Lett.*, 251 (1966); (c) A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Am. Chem. Soc.*, **92,** 5516 (1970).
(6) Review: D. J. Faulkner, *Synthesis*, 175 (1971).
(7) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice Hall, Englewood Cliffs, N.J., 1971, p 375, and references cited therein.
(8) (a) R. K. Hill and N. W. Gilman, *Chem. Commun.*, 619 (1967); (b) R. K. Hill, R. Soman, and S. Sawada, *J. Org. Chem.*, **37,** 3737 (1972), and references cited therein.
(9) (a) A. W. Burgstahler and I. C. Nordin, *J. Am. Chem. Soc.*, **83,** 198 (1961); (b) W. S. Johnson, T. J. Brocksom, P. Loew, D. H. Rich, L. Werthemann, R. A. Arnold, T.-T. Li, and D. J. Faulkner, *ibid.*, **92,** 4463 (1970); (c) W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T.-T. Li, D. J. Faulkner, and M. R. Petersen, *ibid.*, **92,** 741 (1970).
(10) (a) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **26,** 3112 (1961); (b) K. C. Brannock, *J. Am. Chem. Soc.*, **81,** 3379 (1959); (c) P. Cresson, *Bull. Soc. Chim. Fr.*, 2618 (1964); (d) D. S. Sethi, P. Yates, *J. Am. Chem. Soc.*, **95,** 3820 (1973).
(11) W. Watanabe and L. Conlon, *J. Am. Chem. Soc.*, **79,** 2828 (1957).
(12) A. F. Thomas, *J. Am. Chem. Soc.*, **91,** 3281 (1969).
(13) R. Paul, G. Roy, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. Fr.*, 121 (1950).
(14) P. Cresson, *Bull. Soc. Chim. Fr.*, 2629 (1964).
(15) E. J. Corey and J. I. Shulman, *J. Am. Chem. Soc.* **92,** 5522 (1970).
(16) J. E. Bladwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 117 (1973).
(17) (a) P. Golborn and F. Scheinmann, *J. Chem. Soc., Perkin Trans. 1,* 2870 (1973); (b) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **12,** 1566 (1973); (c) E. J. Corey and J. W. Suggs, *J. Org. Chem.*, **38,** 3224 (1973).
(18) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **12,** 2497 (1971).
(19) For example, see J. E. Lyons, *J. Org. Chem.*, **36,** 2497 (1971).
(20) J. Colonge and G. Clerc, *Bull. Soc. Chim. Fr.*, 836 (1955).
(21) For example see: P. S. Bailey, *Ind. Eng. Chem.*, **50,** 993 (1958).
(22) F. A. L. Anet, *Can. J. Chem.*, **39,** 2262 (1961).
(23) M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, **33,** 115 (1941).
(24) B. A. Arbusov and O. N. Nuretdinova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2137 (1963); *Chem. Abstr.*, **60,** 10576e (1964).
(25) F. C. Frostick, Jr., B. Phillips, and P. S. Starcher, *J. Am. Chem. Soc.*, **81,** 3350 (1959).