ligands and trans methyl groups and that 64% have trans-η^5-C_5H_5 ligands and cis methyl groups. A distinction between these explanations is not possible. However, with either assignment complex **10** is unique in that the cis orientation of the methyl groups is the preferred isomer.

The apparent reversal of isomer stability at the aluminum atom of complex **10** may be related to a known trend in isomer stability of non-metallo-β-diketonate complexes and may indicate that electronic effects determine the preferred geometrical isomer.[7,8] As the ring substituents of tris-chelate β-diketonate complexes of aluminum become less electronegative, the trans isomer becomes less stable until the cis isomer finally becomes the more stable isomer. Even though the influence of steric effects on this trend has not been determined, it is tempting to speculate that the ligand of complex **10** might be more basic or electron-rich than the ligand of complex **9** and, therefore, rationalize the enhanced stability of the cis isomer of complex **10**. It is interesting, though perhaps fortuitous, that the enolate proton of complex **6** has the highest field chemical shift observed for any metallo-β-diketone molecule yet prepared.

Acknowledgment. We thank the Research Corporation, the University Research Council of Vanderbilt University, and the generous support of the National Science Foundation (Grant No. CHE-76-14304) for support of this research. We gratefully acknowledge the support of a DuPont fellowship to Jane V. Zeile.

References and Notes

(1) C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, **98**, 2365 (1976).
(2) C. M. Lukehart, G. P. Torrance, and J. V. Zeile, *Inorg. Chem.*, **15**, 2393 (1976).
(3) R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).
(4) C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *J. Am. Chem. Soc.*, **97**, 6903 (1975).
(5) The approximate normal-coordinate analysis of three metallo-β-diketonate complexes has been performed; C. M. Lukehart and G. P. Torrence, submitted for publication.
(6) The statistical proportion of any cis like-group to the analogous trans like-group is still 1:3 as is expected for any unsymmetrical tris-chelate complex which would lack the isomerism generated by the η^5-C_5H_5 ligands of the iron atom.
(7) J. G. Gordon, II, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, **5**, 381 (1971).
(8) C. M. Lukehart and G. P. Torrence, submitted for publication.

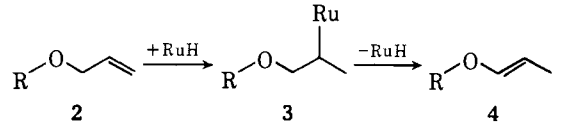
Ruthenium(II) Catalysis in Redox Fragmentation of Allyl Ethers

Robert G. Salomon* and James M. Reuter

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 8, 1976*

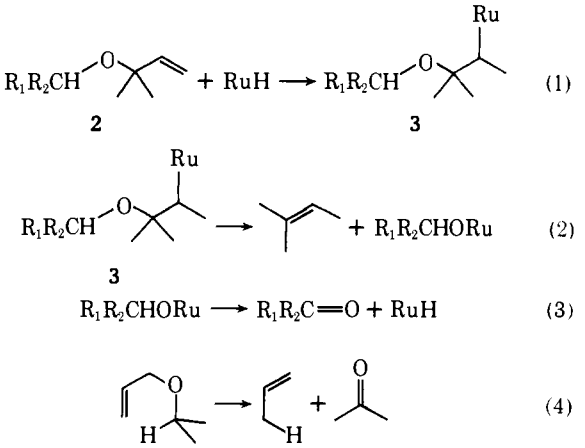
Abstract: A new type of homogeneous transition metal catalyzed process, redox fragmentation of allyl ethers in the presence of tris(triphenylphosphine)ruthenium(II) dichloride (**1**), is reported. α,α-Dimethylallyl benzyl ethers give benzaldehyde and 2-methyl-2-butene. Thus, redox fragmentation is accompanied by allylic transposition of the carbon–carbon double bond. Cleavage of the allylic carbon–oxygen bond is inferred to be rate determining since para substituents on the aryl ring and benzylic deuterium substitution in benzyl ethers have no appreciable effect on the rate of catalyzed fragmentation. Thus, a rate determining elimination of ruthenium(II) alkoxide from a β-alkoxyruthenium(II) intermediate is proposed. Subsequent facile decomposition to carbonyl compound and ruthenium(II) hydride, the actual catalyst of redox fragmentation, is shown to be feasible since sodium benzyl oxide gives benzaldehyde upon reaction with 1 equiv of **1**.

A hydride addition–elimination sequence is considered to account for allylic isomerization of olefins catalyzed by tris(triphenylphosphine)ruthenium(II) dichloride (**1**).[1-3] Thus, allylic ethers **2** yield vinyl ethers **4** via putative intermediate



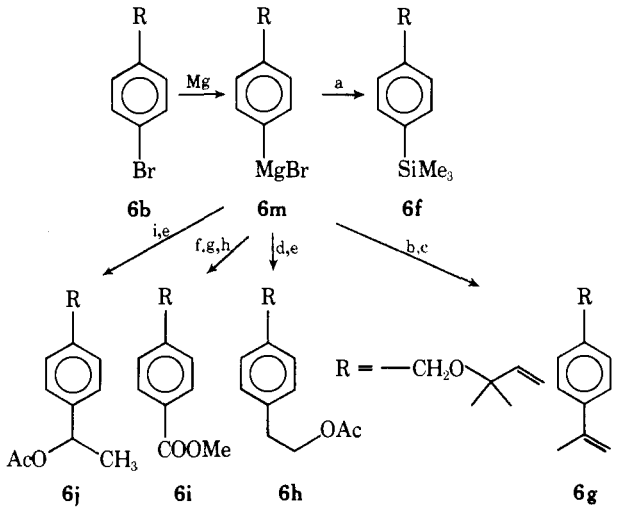
2 **3** **4**

β-alkoxyruthenium alkyls **3**.[4] We speculated that these intermediates might undergo β-elimination of ruthenium alkoxide if β-hydride elimination is precluded by the absence of allylic hydrogen (eq 2). The alkoxides could then eliminate ruthenium hydride[5] to give aldehydes and regenerate the catalyst (eq 3). The overall process (eq 1-3) would be a ruthenium catalyzed redox fragmentation of allylic ethers, and might occur under milder conditions of thermal activation than required for the corresponding retro-ene fragmentation (eq 4).[6] Catalysis would enhance the utility in organic synthesis of such fragmentations since many substrates cannot withstand the thermally harsh conditions (400–500 °C) required for the corresponding uncatalyzed reaction. The reduction of the allyloxy portion and concomitant oxidation of the alkoxy portion of the substrates may both find synthetic applications.



We now report that α,α-dimethylallyl benzyl ethers give benzaldehydes by a new type of homogeneous transition metal catalyzed process, redox fragmentation, in the presence of **1** as catalyst. Furthermore, allyl ethers which have allylic hy-

Scheme I

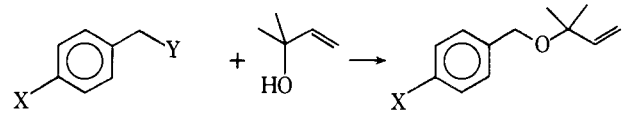


a, Me_3SiCl; b, Me_2CO; c, H^+ ($-H_2O$); d, ⌓; e, Ac_2O, pyridine, f, CO_2; g, H^+, H_2O; h, CH_2N_2; i, MeCHO

drogen also undergo redox fragmentation to give aldehydes or ketones, though this process is much slower than allylic isomerization to give vinyl ethers.

Results

Synthesis of Allyl Ethers. The ethers **6a–e** were prepared by Williamson ether synthesis from the corresponding benzyl halides **5a–e** and 2-methyl-3-buten-2-ol. The ethers **6f–j** were

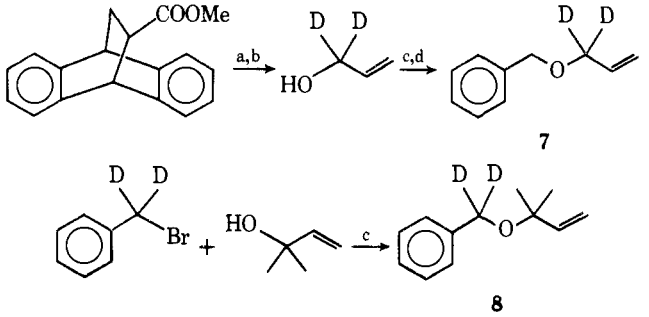


5a, X = H; Y = Br
b, X = Y = Br
c, X = Me; Y = Cl
d, X = OMe; Y = Br
e, X = Cl; Y = Br

6a, X = H
b, X = Br
c, X = Me
d, X = OMe
e, X = Cl

prepared from **6b** via the Grignard reagent **6m** (Scheme I).

Allyl alcohol-α,α-d_2 was prepared via lithium aluminum deuteride reduction of 9,10-dihydro-9,10-(11-carbomethoxyethano)anthracene followed by pyrolysis. The alcohol gave α,α-dideuterioallyl benzyl ether (**7**) upon Williamson etherification with benzyl bromide. Benzyl bromide-α,α-d_2 gave α,α-dimethylallyl benzyl ether-α',α'-d_2 (**8**) by Williamson etherification.



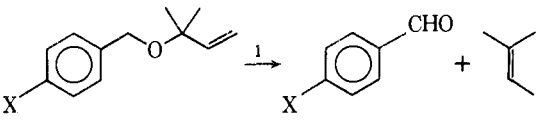
a, $LiAlD_4$; b, 325°C; c, NaH, THF; d, $PhCH_2Br$, HMPA

Allyl cyclododecyl ether (**10**) and allyl cyclopropylcarbinyl ether (**11**) were obtained by allylation of the corresponding alcohols with allyl bromide.

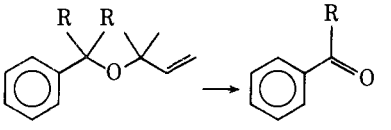
Ruthenium Catalyzed Redox Fragmentation. The ethers **6a–j** were heated under nitrogen under reflux at an oil bath temperature of 200 °C for several hours in the presence of 1 mol % $Ru(PPh_3)_3Cl_2$ (**1**). Yields were determined by ^1H NMR using cyclododecane as internal standard. Products were isolated by preparative gas–liquid phase chromatography and characterized by ^1H NMR and mass spectroscopy (see Experimental Section). In all cases the ethers were cleaved cleanly to yield benzaldehydes **9a–j**. No other major products of similar volatility were produced. The main olefinic product was 2-methyl-2-butene, though traces of isomeric methyl butenes and isoprene were also produced. Yields and relative rates of redox fragmentation, determined by pairwise competition experiments, are given in Table I. The relative rate of catalyzed redox fragmentation of **6a** and the deuterated analogue **8** was determined in a competition experiment and found to be k_H/k_D = 1.1. A minor product (2%) was isolated from the redox fragmentation of **6a** and identified as benzyl *tert*-amyl ether (**12**). Fragmentation is not inhibited by solid $NaHCO_3$.

Table I. Ruthenium Catalyzed Redox Fragmentation of α,α-Dimethylallyl Benzyl Ethers

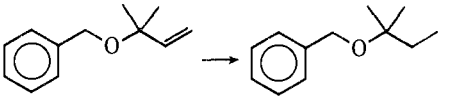
Ether (**6**)	Aldehyde yield, %	Rel rate (k_X/k_H)
a X = H	83	1.00
b X = Br	70	
c X = Me	78	0.94
d X = OMe	73	1.13
e X = Cl	73	1.10
f X = $SiMe_3$	71	
g X = C(Me)=CH_2	63	
h X = CH_2CH_2OAc	66	0.90
i X = CO_2CH_3	68	0.96
j X = $CHOAcCH_3$	65	



6 **9**

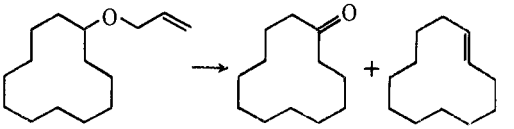


6a, R = H
8, R = D

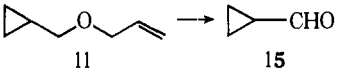


6a **12**

Cyclododecanone (**13**) was obtained in 85% yield from allyloxycyclododecane (**10**) by heating under reflux for 36 h (oil bath 200 °C) in the presence of 0.25 mol % of $Ru(PPh_3)_3Cl_2$ (**1**). A minor product (13% yield), cyclododecene (**14**), was also produced in the reaction. Similarly, allyl cyclopropylcarbinyl ether (**11**) gave cyclopropanecarboxaldehyde (**15**) upon heating at 200 °C for 48 h in a sealed tube in the presence of 0.25 mol % of **1**. Both **10** and **11** are rapidly isomerized to the



10 **13** (85%) **14** (13%)



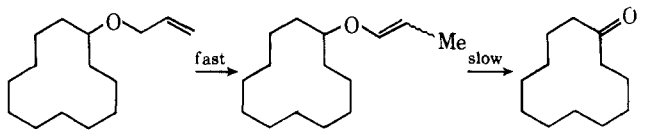
11 **15**

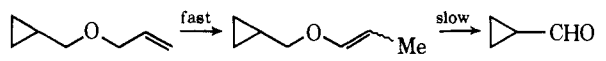
Table II. Parent Region of Mass Spectrum Showing Intermolecular H–D Exchange during Ruthenium Catalyzed Isomerization of Allyl Ethers

Ether[a]	*m/e* (rel intensity) Parent-d_0		Parent-d_2
7-d_2	148 (2)	149 (16)	150 (17)
21	148 (9)	149 (16)	150 (0.2)
22	162 (11)	163 (17)	164 (13)
23-d_0	162 (21)	163 (3)	164 (0.5)

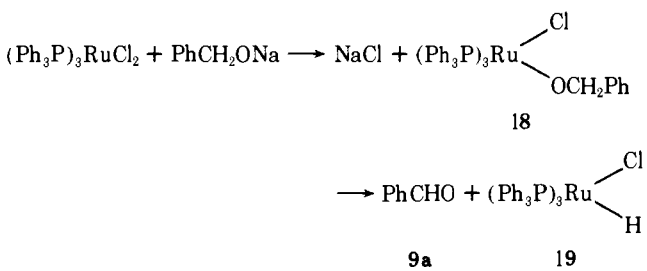
[a] See text.

corresponding propenyl ethers **16** and **17**, respectively, upon heating in the presence of **1**. The propenyl ethers were isolated and then cleaved to **13** and **15** by heating in the presence of **1** at higher temperatures.



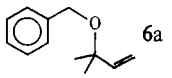


Decomposition of a Ruthenium Benzyl Oxide Complex. To test the feasibility of the last step of the mechanism of eq 1–3, we examined the reaction of sodium benzyl oxide with 1 equiv of ruthenium complex **1** at room temperature. Benzaldehyde (**9a**) was obtained in 84% yield, presumably by elimination of a ruthenium hydride **19** from an intermediate ruthenium benzyl oxide complex **18**.[7]

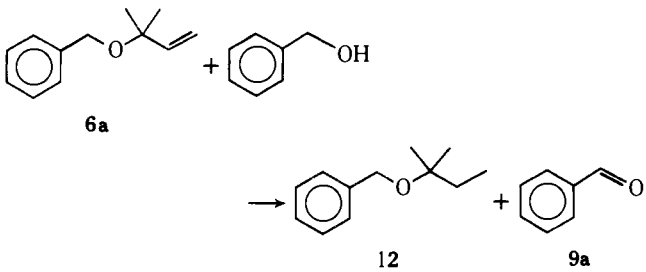


Intermolecular H–D Exchange during Ruthenium Catalyzed Allylic Isomerization of Allyl Ethers. An addition–elimination mechanism is considered to be operative for allylic isomerization of olefins catalyzed by **1**.[1-3] Such a mechanism predicts exchange of hydrogen atoms between the olefin and a ruthenium hydride catalyst generated in situ and hence intermolecular exchange of hydrogen atoms between molecules of olefin. In order to determine whether such exchange occurs during the isomerization of allyl ethers into vinyl ethers, a mixture of the deuterated ether **7** and 10 equiv of allyl *p*-methylbenzyl ether (**20**) was isomerized in the presence of **1**. The parent peak region of the mass spectrum of the benzyl propenyl ether (**21**) produced is given in Table II together with that of **7**. Also, a mixture containing **20** and 10 equiv of **7** was isomerized in the presence of **1**. The parent peak region of the mass spectrum of the *p*-methylbenzyl propenyl ether (**22**) produced is given in Table II together with that of an authentic sample of undeuterated *p*-methylbenzyl propenyl ether (**23**). Clearly, **21** contains little or no d_2 and appreciable d_0 benzyl propenyl ether. In contrast, **22** contains appreciable d_1 and d_2 *p*-methylbenzyl propenyl ether. Thus, allylic hydrogen and deuterium are exchanged intermolecularly during ruthenium catalyzed isomerization of allyl ethers.

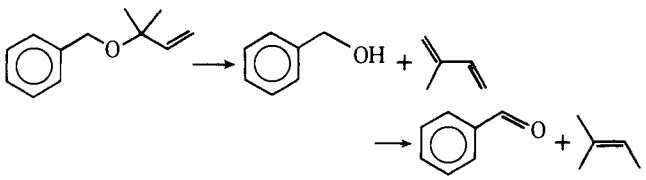
Table III. Relative Yields of Methylbutenes from Redox Fragmentation of **6a** and Transfer Hydrogenation of Isoprene

Starting material	Products, mol %		
 **6a**	92	6	2
	65	30	5

Ruthenium Catalyzed Transfer Hydrogenation of 6a with Benzyl Alcohol. A possible source of the reduced by-product **12** is ruthenium catalyzed transfer hydrogenation of **6a**. Indeed, heating **6a** in the presence of benzyl alcohol gave **12** quantitatively along with an equivalent amount of benzaldehyde (**9a**) as the exclusive products.



Ruthenium Catalyzed Transfer Hydrogenation of Isoprene with Benzyl Alcohol. The possibility was considered that redox fragmentation of benzyl α,α-dimethylallyl ethers results from preliminary elimination of benzyl alcohol to yield isoprene followed by hydrogen transfer to give benzaldehyde and 2-methyl-2-butene. Therefore, isoprene and benzyl alcohol were heated in the presence of 1 mol % of catalyst **1**. After 12 h of



heating with an oil bath temperature of 200 °C under reflux under nitrogen, a 43% conversion to methylbutenes was observed. The ratio of products is compared in Table III with the ratio of methylbutenes produced during redox fragmentation of benzyl α,α-dimethylallyl ether catalyzed by **1** under similar reaction conditions.

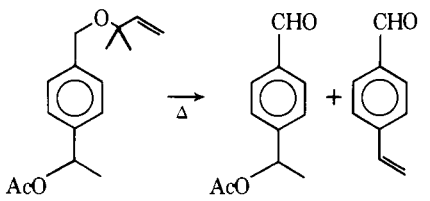
In a control experiment, 2-methyl-2-butene was heated in the presence of 1 mol % of catalyst **1** and a 9:1 mixture of benzaldehyde and benzyl alcohol under reflux under nitrogen for 12 h at an oil bath temperature of 200 °C. No rearrangement to isomeric methylbutenes occurred. Catalytic activity similar to that of **1** for redox fragmentation of allyl ethers was also observed for dihydridocarbonyltris(triphenylphosphine)ruthenium(II)[8] and chlorohydridocarbonyltris(triphenylphosphine)ruthenium(II).[9]

Discussion

Synthetic Applications. The ruthenium catalyzed redox fragmentation reaction disclosed in this report is a new type of homogeneous transition metal catalyzed process. Several aspects of the process merit consideration regarding synthetic applications. The direct transformation of allyl ethers into carbonyl compounds makes the former synthetic equivalents of the latter. That is, allyl ethers may be employed as latent carbonyl groups[10] which would be unaffected by a variety of

oxidizing and reducing agents as well as organometallic reagents. The latter possibility is demonstrated in Scheme I in which the Grignard reagent **6m** leads to a variety of benzaldehydes after deblocking.

Since some functional groups are thermally unstable, the catalyzed fragmentation enjoys a synthetically useful advantage over the uncatalyzed process which requires considerably harsher conditions of thermal activation.[6] Thus, thermal fragmentation of the acetate **6j** is accompanied by some elimination of acetic acid. Even under carefully controlled conditions which just suffice to induce 99% completion of fragmentation, the products consisted of 74% acetoxyaldehyde **9j** and 25% vinylaldehyde **9k** (see Experimental Section). No vinylaldehyde formation accompanied the ruthenium catalyzed

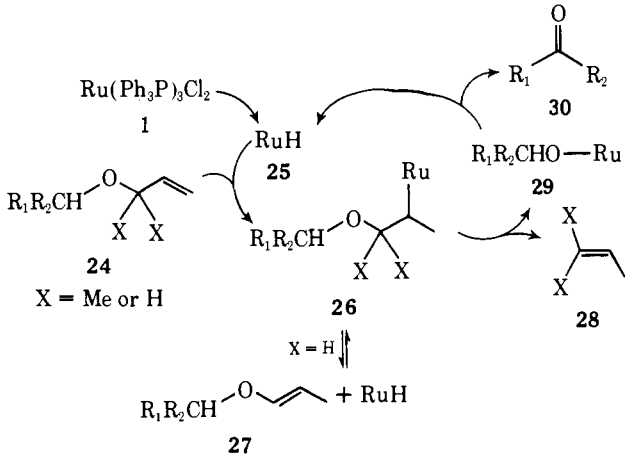


6j **9j** **9k**

redox fragmentation of **6j** to **9j**. Nevertheless, catalysts which promote redox fragmentation under even milder conditions should be one goal of future research on this reaction.

Mechanism. A mechanism presented in Scheme II, involving

Scheme II



a rate-determining β-elimination of ruthenium alkoxide, can account for the catalyzed redox fragmentation. The absence of an appreciable substituent effect (Table I) or kinetic isotope effect in the catalyzed fragmentation of **6** and **8**, respectively, suggests that benzylic C–H bond cleavage is not rate determining. In agreement with this requirement, benzaldehyde was readily obtained at room temperature from the reaction of sodium benzyloxide with **1**. Thus, decomposition of the putative ruthenium alkoxide intermediate **29** would be very rapid under the fragmentation reaction conditions.[5,7]

Since **26** is a mandatory intermediate in the allylic isomerization of **24** (X = H) catalyzed by ruthenium, and since allylic isomerization is rapid relative to redox fragmentation, it follows that formation of **26** by addition of ruthenium hydride **25** to **24** or **27** is rapid and reversible. Therefore, β-elimination of ruthenium alkoxide **29** from **26** must be rate determining. The intermolecular H–D exchange observed during isomerization of allyl to propenyl ethers catalyzed by ruthenium suggests a hydride addition elimination mechanism for this isomerization, and supports the postulated formation of a ruthenium hydride species from the nominal catalyst **1** as the actual catalyst of redox fragmentation, though this was not demonstrated directly.[11] This analysis suggests that future research on the development of catalysts for redox fragmentation under milder, more synthetically attractive reaction conditions should focus on the metal alkoxide elimination step. The reaction of allyl ethers with other transition metal catalysts, such as cobalt,[12] iron,[13] and zirconium[14] hydrides which catalyze isomerization of olefins by an addition-elimination sequence should be explored. Hydrides which add to (reduce) carbonyl groups (e.g., boron or aluminum hydrides), of course, cannot catalyze redox fragmentation.

Since HCl might be generated during the postulated conversion of **1** to a ruthenium hydride species, HCl might catalyze elimination of benzyl alcohol. But an alternative mechanism for redox fragmentation involving preliminary elimination of benzyl alcohol to give isoprene, followed by hydrogen transfer from benzyl alcohol to the diene, is unlikely for two reasons. First, when the volatile olefinic products from redox fragmentation of **6a** were continuously swept from the reaction mixture during the reaction with a slow stream of nitrogen, only 10% of the olefinic products was isoprene. Also, transfer hydrogenation of isoprene with benzyl alcohol gives five times more 2-methyl-1-butene than is obtained from the redox fragmentation of **6a** (Table III). Furthermore, solid $NaHCO_3$, which would sequester any adventitious protic acid, did not inhibit fragmentation.

The formation of **12** from **6a** undoubtedly involves hydrogen transfer catalyzed by ruthenium.[15] The hydrogen source may be 3-methylbutene-2 leading to formation of isoprene. Traces of isoprene were identified in the reaction product mixture. Alternatively, isoprene may arise directly from **6a** by elimination of benzyl alcohol. The latter, we have shown, readily transfers hydrogen to **6a** in the presence of **1** as catalyst.

Conclusions

Fragmentation of α,α-dimethylallyl benzyl ethers (**6**) to give benzaldehydes and 2-methyl-2-butene is catalyzed by tris(triphenylphosphine)ruthenium dichloride (**1**). Since the reaction tolerates a wide variety of substituents on the aromatic ring, the ethers (**6**) may be used in synthesis as latent benzaldehydes.

Cleavage of the benzylic C–H bond occurs after the rate-determining step and the reaction does not exhibit a substituent effect on rate. A mechanism which can account for the catalysis is related to the mechanism by which **1** catalyzes allylic rearrangement of olefins.

Though the identity of the actual catalyst is unknown, it is probably a ruthenium hydride species which is generated in situ from the nominal ruthenium dichloride catalyst. Addition of the hydride to the C–C double bond of the allyl group gives an organoruthenium(II) derivative with a vicinal alkoxy substituent. This intermediate undergoes a rate-determining β-elimination of ruthenium alkoxide. The latter decomposes to benzaldehyde and regenerates the ruthenium hydride catalyst. Allyl ethers which have allylic hydrogen also undergo redox fragmentation, though allylic isomerization to give vinyl ethers is much faster.

Experimental Section

General. Reactions were carried out in flame-dried flasks under an atmosphere of N_2. Analytical gas–liquid phase chromatography was performed with a Varian Model 1400 chromatograph with flame ionization detector using a 5 ft × 0.125 in. column containing 1.5% O.V. (methyl silicone) on Chromosorb W at 180 °C unless otherwise indicated. Proton magnetic resonance spectra were recorded with a Varian A-60A or HA-100 FT spectrometer with tetramethylsilane (1.5%) as internal standard and CCl_4 as solvent. Mass spectra were determined with a Du Pont Model 21-094 GC/MS with computer analysis. Boiling points were uncorrected. Melting points were measured with a Thomas-Hoover capillary melting point apparatus. El-

emental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Synthesis of Ethers. Williamson Method. 3-Benzyloxy-3-methyl-1-butene (6a). Sodium hydride (9.12 g, 0.39 mol, 57% oil dispersion) in a 250-mL three-neck flask equipped with mechanical stirrer, reflux condenser, and addition funnel was washed with pentane (2 × 50 mL). Then THF (100 mL), freshly distilled from sodium benzophenone ketyl, was added, followed by the careful addition of 3-methyl-3-hydroxy-1-butene (14.7 g, 0.17 mol). The resulting mixture was boiled under reflux until H_2 evolution ceased (2 h). While the mixture was still warm, HMPA (80 mL) was added in one portion, followed by cautious, portionwise addition of benzyl bromide (23.5 mL, 0.17 mol) (exothermic) at such a rate as to maintain a gentle reflux. The reaction mixture was boiled under reflux for an additional 3 h, cooled, and quenched with 10% HCl (50 mL), and the product extracted with pentane (2 × 100 mL). The combined organic extracts were washed with 10% HCl (50 mL), saturated $NaHCO_3$ (50 mL), H_2O (50 mL), and saturated NaCl (50 mL), and dried ($MgSO_4$). Solvent was removed by rotary evaporation and the crude product carefully distilled. Yields and physical constants for the title ether, and ethers prepared similarly, are listed below: ether (yield, bp) **6a** (70%, 85–86 °C (1.85 mm)); **6b** (91%, 93–95 °C (0.07 mm)); **6c** (84%, 74 °C (1.40 mm)); **6d** (86%, 95 °C (1.13 mm)); **63** (84%, 85 °C (0.95 mm)); **22** (73%, 94–96 °C (1.25 mm)); **10** (87%, 115 °C (0.74 mm)); **11** (76%, 118–125 °C).

Proton Magnetic Resonance and Mass Spectra. 3-Benzyloxy-3-methyl-1-butene (6a). ^1H NMR δ 1.30 (6 H, s, CH_3), 4.32 (2 H, s, CH_2), 4.93–5.32 (2 H, m, vinyl CH_2), 5.92 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.21 (5 H, s, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (13), 91 (100), 138 (49), 176 (19).

3-(*p*-Bromobenzyloxy)-3-methyl-1-butene (6b). ^1H NMR δ 1.32 (6 H, s, CH_3), 4.27 (2 H, s, CH_2), 4.94–5.30 (2 H, m, vinyl CH_2), 5.88 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.12 (2 H, d, J = 8.5 Hz, aryl), 7.39 (2 H, d, J = 8.5 Hz, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (43), 106 (25), 158 (100), 174 (22), 245 (18).

Anal. ($C_{12}H_{15}BrO$) C, H.

3-(*p*-Methylbenzyloxy)-3-methyl-1-butene (6c). ^1H NMR δ 1.28 (6 H, s, CH_3), 2.18 (3 H, s, CH_3), 4.27 (2 H, s, CH_2), 4.93–5.30 (2 H, m, vinyl CH_2), 5.89 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.07 (4 H, s, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (46), 91 (100), 106 (53), 148 (8), 180 (5).

Anal. ($C_{13}H_{18}O$) C, H.

3-(*p*-Methoxybenzyloxy)-3-methyl-1-butene (6d). ^1H NMR δ 1.28 (6 H, s, CH_3), 3.65 (3 H, s, CH_3), 4.20 (2 H, s, CH_2), 4.90–5.28 (2 H, m, vinyl CH_2), 5.89 (1 H, dd, J = 10, 18 Hz, vinyl CH), 6.72 (2 H, d, J = 8.5 Hz, aryl), 7.14 (2 H, d, J = 8.5 Hz, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (33), 91 (41), 121 (100), 291 (20), 206 (7).

Anal. ($C_{13}H_{18}O_2$) C, H.

3-(*p*-Chlorobenzyloxy)-3-methyl-1-butene (6e). ^1H NMR δ 1.32 (6 H, s, CH_3), 4.27 (2 H, s, CH_2), 4.94–5.30 (2 H, m, vinyl CH_2), 5.87 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.13 (2 H, d, J = 8.0 Hz, aryl), 7.39 (2 H, d, J = 8.0 Hz, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (51), 105 (25), 158 (100), 140 (32), 211 (14).

Anal. ($C_{12}H_{15}ClO$) C, H.

Allyl *p*-Methylbenzyl Ether (20). ^1H NMR δ 2.23 (3 H, s, CH_3), 3.88 (2 H, dt, J = 1, 4 Hz, CH_2), 4.34 (2 H, s, CH_2), 4.9–5.4 (2 H, m, vinyl CH_2), 5.5–6.2 (1 H, m, vinyl CH), 7.05 (4 H, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 65 (10), 77 (27), 78 (10), 79 (12), 91 (34), 93 (18), 103 (11), 105 (100), 106 (66), 119 (27), 120 (41), 121 (14), 132 (10), 162 (18).

Anal. ($C_{11}H_{14}O$) C, H.

Allyl Cyclododecyl Ether (10). ^1H NMR δ 1.37 (22 H, s, ring CH_2), 3.18–3.53 (1 H, broad s, CH), 3.89 (2 H, dt, J = 1, 5 Hz, CH_2), 4.86–5.38 (2 H, m, vinyl CH_2), 5.53 (1 H, m, vinyl CH); mass spectrum (70 eV) *m/e* (rel intensity) 69 (48), 81 (42), 82 (56), 83 (52), 84 (43), 95 (41), 96 (38), 97 (61), 98 (35), 109 (28), 111 (31), 166 (60), 167 (42), 224 (33).

Anal. ($C_{15}H_{28}O$) C, H.

Allyl Cyclopropylcarbinyl Ether (11). ^1H NMR δ 0.10–0.62 (4 H, m, cyclopropyl CH_2), 0.78–1.20 (1 H, m, CH), 3.44 (2 H, t, J = 6 Hz, CH_2), 2.39 (2 H, dt, J = 1, 5 Hz, CH_2), 4.85–5.38 (2 H, m, vinyl CH_2), 5.53–6.19 (1 H, m, vinyl CH); mass spectrum (70 eV) *m/e* (rel intensity) 55 (100), 56 (15), 59 (16), 70 (11), 74 (12), 84 (12), 85 (12), 112 (73).

Anal. ($C_7H_{12}O$) C, H.

Synthesis of Ethers. Grignard Method. *p*-(3-Methyl-1-butenyl-3-oxymethyl)phenylmagnesium Bromide (6m). To a 250-mL three-neck flask, fitted with reflux condenser, addition funnel, and mechanical stirrer, was added magnesium turnings (0.95 g, 0.04 mol) and THF (10 mL). Then 3-(*p*-bromobenzyloxy)-3-methyl-1-butene (4.0 g, 0.02 mol) in THF (50 mL) was added portionwise with stirring. Gentle heating to reflux with a flame was sufficient to start the reaction. After addition was complete the mixture was boiled under reflux for 3 h and then allowed to cool.

A. 3-(*p*-Trimethylsilylbenzyloxy)-3-methyl-1-butene (6f). To **6m** was added portionwise chlorotrimethylsilane (2.5 g, 0.02 mol) in THF (20 mL) with vigorous mechanical stirring. After addition the mixture was boiled overnight under reflux, cooled, and washed into a separatory funnel with ether taking care to leave unreacted magnesium behind. The reaction was quenched with 10% HCl (50 ml) and the aqueous layer extracted with ether (2 × 50 mL). The combined organic extracts were washed with 10% HCl (50 mL), saturated $NaHCO_3$ (50 mL), water (50 mL), and saturated NaCl (50 mL), and dried ($MgSO_4$). The solvent was stripped by rotary evaporation and the product carefully distilled to yield **6f** (93%): bp 135–136 °C (0.85 mm); ^1H NMR δ 0.26 (9 H, s, CH_3), 1.32 (6 H, s, CH_3), 4.32 (2 H, s, CH_2), 4.95–5.32 (2 H, m, vinyl CH_2), 5.91 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.18 (2 H, d, J = 8 Hz, aryl), 7.41 (2 H, d, J = 8 Hz, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (66), 91 (22), 135 (34), 163 (100), 249 (9).

Anal. ($C_{15}H_{24}OSi$) C, H.

The procedure for the synthesis of the remaining Grignard adducts was identical with the one described above except that in place of chlorotrimethylsilane, the following substitutions were made: for **6g**, dimethyl ketone; for **6h**, ethylene oxide; for **6i**, CO_2; for **6j**, acetaldehyde. The initial adducts: 3-[*p*-(1-methyl-1-hydroxy)ethyl]benzyloxy-3-methyl-1-butene, bp 132 °C (0.4 mm) (68%); 3[*p*-(β-hydroxy)ethyl]benzyloxy-3-methyl-1-butene, bp 131 °C (0.5 mm) (81%); 3-(*p*-carboxy)benzyloxy-3-methyl-1-butene (78%); and 3-[*p*-(α-hydroxy)ethyl]benzyloxy-3-methyl-1-butene, bp 122 °C (0.2 mm) (76%), respectively, were transformed into the final products **6g–j** according to the following procedures.

B. 3-(*p*-Isopropenylbenzyloxy)-3-methyl-1-butene (6g). 3-(*p*-1-Methyl-1-hydroxyethylbenzyloxy)-3-methyl-1-butene (3.1 g, 0.01 mol) in benzene (25 mL) with a catalytic amount of *p*-toluenesulfonic acid (25 mg) was boiled under reflux for 3 min and the reaction quenched immediately with saturated $NaHCO_3$ (50 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation. Distillation gave **6g** (83% overall): bp 86 °C (1.40 mm); ^1H NMR δ 1.32 (6 H, s, CH_3), 2.11 (3 H, d, J = 1 Hz, CH_3), 4.30 (2 H, s, CH_2), 4.93–5.33 (4 H, m, vinyl CH_2, vinyl CH_2), 5.90 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.17 (2 H, d, J = 8.5 Hz, aryl), 7.35 (2 H, d, J = 8.5 Hz, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (36), 91 (32), 131 (100), 147 (65), 216 (41).

Anal. ($C_{15}H_{20}O$) C, H.

C. 3-[*p*-(β-Acetoxy)ethylbenzyloxy]-3-methyl-1-butene (6h). To 3-[*p*-(β-hydroxy)ethyl]benzyloxy-3-methyl-1-butene (0.5 g, 2.27 mmol) and acetic anhydride (3.0 g, 0.03 mol) was added anhydrous pyridine (2.0 g, 0.02 mol). The solution was heated at 60 °C for 6 h and then stirred at room temperature overnight. The mixture was taken up in ether and washed with saturated $NaHCO_3$ (24 mL), 10% HCl (25 mL), water (25 mL), and saturated NaCl (25 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product eluted through silica gel (20 g, 60–200 mesh) with CCl_4 to give **6h** after evaporation of solvent (80% overall), bp 120 °C (0.25 mm): ^1H NMR δ 1.30 (6 H, s, CH_3), 1.80 (3 H, s, ester), 2.85 (2 H, t, J = 7 Hz, CH_2), 4.13 (2 H, t, J = 7 Hz, CH_2), 4.30 (2 H, s, CH_2), 4.93–5.33 (2 H, m, vinyl CH_2), 5.90 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.07 (4 H, s, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (35), 91 (32), 191 (6), 193 (100), 263 (37), 278 (10).

Anal. ($C_{16}H_{22}O_3$) C, H.

D. 3-(*p*-Carbomethoxybenzyloxy)-3-methyl-1-butene (6i). To 3-(*p*-carboxybenzyloxy)-3-methyl-1-butene in ether was added an excess of freshly prepared diazomethane in ether. The mixture was stirred at room temperature for 1 h. The solvent was stripped by rotary evaporation to give **6i** (76% overall): bp 127 °C (0.98 mm); ^1H NMR δ 1.32 (6 H, s, CH_3), 3.84 (3 H, s, CH_3), 4.38 (2 H, s, CH_2), 4.94–5.31 (2 H, m, vinyl CH_2), 5.89 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.27 (2 H, d, J = 8 Hz, aryl), 7.93 (2 H, d, J = 8 Hz, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 70 (73), 91 (15), 149 (100), 203 (17), 234 (3).

Anal. ($C_{14}H_{18}O_3$) C, H.

E. 3-[*p*-(α-Acetoxy)ethylbenzyloxy]-3-methyl-1-butene (6j). To 3-[*p*-(α-hydroxy)ethyl]benzyloxy-3-methyl-1-butene (0.5 g, 2.27 mol) and acetic anhydride (3.0 g, 0.03 mol) was added anhydrous pyridine (2.0 g, 0.02 mol). The solution was heated at 60 °C for 6 h and then stirred at room temperature overnight. The mixture was taken up in ether and washed with saturated $NaHCO_3$ (25 mL), 10% HCl (25 mL), water (25 mL), and saturated NaCl (25 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product vacuum transferred to give **6j** in 87% yield: ^{1}H NMR δ 1.32 (6 H, s, CH_3), 1.48 (3 H, d, J = 6.5 Hz, CH_3), 1.97 (3 H, s, CH_3), 4.32 (2 H, s, CH_2), 4.90–5.31 (2 H, m, vinyl CH_2), 5.63–6.16 (2 H, m, CH, vinyl CH), 7.21 (4 H, s, aryl).

Anal. ($C_{16}H_{22}O_3$) C, H.

9,10-Dihydro-9,10-(11-dideuteriohydroxymethylethano)anthracene. A 100-mL three-neck Morton flask, fitted with reflux condenser, mechanical stirrer, and addition funnel, was charged with $LiAlD_4$ (1.0 g, 0.02 mol) and ether (50 mL) freshly distilled from $LiAlH_4$. To this stirred mixture was cautiously added 9,10-dihydro-9,10-(11-carbomethoxyethano)anthracene[16] (12.4 g, 0.47 mol) in ether (25 mL). After completion of the addition, the mixture was stirred under reflux for 5 h, then cooled to room temperature, and quenched with water (1 mL), 15% NaOH (2 mL), and water (1 mL), respectively. The solid residue was filtered and washed thoroughly with ether. The combined organic fractions were washed with saturated $NaHCO_3$ (100 mL) and brine (100 mL), and dried ($MgSO_4$). The solvent was stripped by rotary evaporation yielding the title product (11.3 g, 92%, mp 103–105 °C): ^{1}H NMR δ 1.95–2.37 (2 H, m, CH_3), 2.63–2.95 (1 H, m, CH), 3.37–3.45 (1 H, broad s, OH), 4.12 (1 H, t, J = 2.0 Hz, CH), 4.28 (1 H, d, J = 2.0 Hz, CH), 6.84–7.30 (8 H, m, aromatic).

α,α-d_2-Allyl Alcohol. 9,10-Dihydro-9,10-(11-dideuteriohydroxymethylethano)anthracene (10.4 g, 0.04 mol) was placed in a 20-mL round-bottom flask fitted with short path distillation head and dry ice–acetone cooled receiver. Then a lead metal bath at 325 °C was raised to the flask until the solid melted and then raised further to maintain a gentle reflux. Heating was continued for 0.5 h. The crude product was eluted through silica gel (20 g, 60–200 mesh) with CCl_4 and the solution carefully distilled to yield the title alcohol (1.5 g, 43%, bp 96–98 °C): ^{1}H NMR δ 3.58–3.76 (1 H, broad s, OH), 4.94–5.40 (2 H, m, vinyl CH_2), 5.96 (1 H, dd, J = 10, 18 Hz, vinyl CH).

α,α-Dideuterioallyl Benzyl Ether (7). α,α-d_2-Allyl alcohol gave α,α-dideuterioallyl benzyl ether (**7**) upon Williamson etherification (bp 85–87 °C, 5.7 mm): ^{1}H NMR δ 4.46 (2 H, s, CH_2), 5.00–5.43 (2 H, m, vinyl CH_2), 5.93 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.26 (5 H, s, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 43 (28), 65 (31), 91 (100), 105 (42), 150 (19).

α,α-Dimethylallyl Benzyl Ether-α′,α′-d_2 (8). α,α-Dideuteriobenzyl bromide[17] gave α,α-dimethylallyl benzyl ether-α′,α′-d_2 (**8**) by Williamson etherification (bp 85–86 °C, (1.9 mm): ^{1}H NMR δ 1.34 (6 H, s, CH_3), 4.94–5.30 (2 H, m, vinyl CH_2), 5.88 (1 H, dd, J = 8, 18 Hz, vinyl CH), 7.18 (5 H, s, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 71 (15), 91 (68), 92 (100), 140 (53), 178 (5).

Ruthenium Catalyzed Redox Fragmentation of Benzyl α,α-Dimethylallyl Ethers. Benzaldehyde (9a). 3-Benzyloxy-3-methyl-1-butene (**6a**, 500 mg, 2.83 mmol) and tris(triphenylphosphine)ruthenium dichloride (**1**, 27.8 mg, 1 mol %), with cyclododecane (11.4 mg, 0.68 mmol) as NMR internal standard, were placed in a 10-mL round-bottom flask fitted with reflux condenser. The contents were heated at 200 °C in an oil bath for 30 h yielding benzaldehyde (83%). On a preparative scale, 7.0 g (0.04 mol) of **6a** with 1 mol % of **1** was converted in an 74% isolated yield to benzaldehyde: ^{1}H NMR δ 7.25–8.26 (5 H, m, aryl), 10.00 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 33 (21), 92 (100), 106 (16).

Ethers **6a–i** were converted to their corresponding aldehydes using the procedure described above. Spectra of the aldehydic products, which follow immediately, were identical with those of authentic samples.

***p*-Bromobenzaldehyde (9b).** ^{1}H NMR δ 7.50 (2 H, d, J = 9 Hz, aryl), 7.75 (2 H, d, J = 9 Hz, aryl), 9.97 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 41 (51), 61 (24), 106 (100), 144 (24), 185 (14).

***p*-Methylbenzaldehyde (9c).** ^{1}H NMR δ 2.16 (3 H, s, CH_3), 7.24 (2 H, d, J = 8 Hz, aryl), 7.66 (2 H, d, J = 8 Hz, aryl), 9.80 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 91 (52), 106 (100), 122 (19).

***p*-Methoxybenzaldehyde (9d).** ^{1}H NMR δ 3.65 (3 H, s, CH_3), 6.52 (2 H, d, J = 9 Hz, aryl), 7.42 (2 H, d, J = 9 Hz, aryl), 10.01 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 90 (43), 106 (100), 136 (12).

***p*-Chlorobenzaldehyde (9e).** ^{1}H NMR δ 7.53 (2 H, d, J = 9 Hz, aryl), 7.75 (2 H, d, J = 9 Hz, aryl), 10.10 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 41 (38), 61 (14), 106 (100), 141 (6).

***p*-Trimethylsilylbenzaldehyde (9f).** ^{1}H NMR δ 0.31 (9 H, s, CH_3), 7.48 (2 H, d, J = 8 Hz, aryl), 8.04 (2 H, d, J = 8 Hz, aryl), 9.96 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 73 (2), 150 (100), 151 (127), 166 (17).

***p*-Isopropenylbenzaldehyde (9g).** ^{1}H NMR δ 2.11 (3 H, d, J = 0.8 Hz, CH_3), 5.40 (2 H, broad d, J = 2.5 Hz, vinyl CH_2), 7.62 (2 H, d, J = 9 Hz, aryl), 7.87 (2 H, d, J = 9 Hz, aryl), 10.03 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 90 (28), 130 (100), 146 (49).

***p*-(β-Acetoxyethyl)benzaldehyde (9h).** ^{1}H NMR δ 1.80 (3 H, s, CH_3), 2.85 (2 H, t, J = 7 Hz, CH_2), 4.13 (2 H, t, J = 7 Hz, CH_2), 7.22 (2 H, d, J = 8 Hz, aryl), 7.64 (2 H, d, J = 8 Hz, aryl), 9.78 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 90 (31), 132 (23), 165 (100), 180 (27).

Anal. ($C_{11}H_{12}O$) C, H.

***p*-Carbomethoxybenzaldehyde (9i).** ^{1}H NMR δ 3.98 (3 H, s, ester CH_3), 7.99 (2 H, d, J = 3 Hz, aryl), 8.17 (2 H, d, J = 3 Hz, aryl), 10.11 (1 H, s, CHO); mass spectrum (70 eV) *m/e* (rel intensity) 44 (15), 90 (25), 105 (32), 149 (100), 164 (24).

***p*-(α-Acetoxy)ethylbenzaldehyde (9j).** ^{1}H NMR δ 1.52 (3 H, d, J = 6.5 Hz, CH_3), 2.02 (3 H, s, CH_3), 5.85 (1 H, q, J = 6 Hz, CH), 7.39 (2 H, d, J = 8 Hz, aryl), 7.78 (2 H, d, J = 8 Hz, aryl), 9.90 (1 H, s, CHO).

Anal. ($C_{11}H_{12}O_3$) C, H.

Ruthenium Catalyzed Allylic Rearrangement of Allyl Ethers. Cyclododecyl 1-Propenyl Ether (16). Cyclododecyl allyl ether (**10**, 500 mg, 2.23 mmol) and tris(triphenylphosphine)ruthenium dichloride (**1**, 2.0 mg, 0.25 mol %) were heated in an NMR tube in a 200 °C oil bath for 15 min. The product was then vacuum transferred to remove the catalyst and analyzed by NMR (100% yield): ^{1}H NMR δ 1.06–1.80 (25 H, large broad s, CH_3, ring CH_2), 3.48–3.89 (1 H, broad s, CH), 4.00–4.80 (1 H, m, vinyl CH), 5.68–6.80 (1 H, m, vinyl CH); mass spectrum (70 eV) *m/e* (rel intensity) 41 (72), 43 (39), 55 (86), 57 (29), 58 (51), 67 (34), 69 (56), 81 (30), 82 (59), 83 (53), 96 (65), 97 (48), 166 (100), 224 (50).

Anal. ($C_{15}H_{28}O$) C, H.

Cyclopropylmethyl 1-Propenyl Ether (17). Cyclopropylmethyl allyl ether (**11**, 5.0 g, 0.04 mol) and tris(triphenylphosphine)ruthenium dichloride (**1**, 45 mg, 0.1 mol %) were boiled under reflux for 12 h. The product was vacuum transferred to remove the catalyst (100% yield): ^{1}H NMR δ 0.10–0.64 (4 H, m, cyclopropyl CH_2), 0.78–1.20 (1 H, m, cyclopropyl CH), 1.53 (3 H, dd, J = 0.2, 5 Hz, CH_3), 3.44 (2 H, t, J = 6 Hz, CH_2), 3.98–4.80 (1 H, m, vinyl CH), 5.70–6.28 (1 H, m, vinyl CH); mass spectrum (70 eV) *m/e* (rel intensity) 39 (34), 41 (16), 53 (13), 55 (100), 56 (12), 57 (13), 58 (19), 70 (29), 112 (33).

Anal. ($C_7H_{12}O$) C, H.

***p*-Methylbenzyl 1-Propenyl Ether (23).** Allyl *p*-methylbenzyl ether (**20**) was isomerized as for the preparation of **16** from **10** above: ^{1}H NMR δ 2.30 (3 H, s, CH_3), 3.92 (2 H, dt, J = 1.3, 5 Hz, CH_2), 4.39 (2 H, s, CH_2), 4.96–5.44 (2 H, m, vinyl CH_2), 5.50–6.25 (1 H, m, vinyl CH), 7.10 (4 H, s, aryl); mass spectrum (70 eV) *m/e* (rel intensity) 77 (27), 91 (45), 105 (100), 120 (45), 162 (21).

Anal. ($C_{11}H_{14}O$) C, H.

Ruthenium Catalyzed Redox Fragmentation of Allyl Ethers. Cyclododecanone (13). Cyclododecyl allyl ether (**10**, 2.0 g, 8.91 mmol) and tris(triphenylphosphine)ruthenium dichloride (**1**, 23 mg, 0.25 mol %) were heated in a one-piece round-bottom flask with reflux condenser and stopcock for removal of aliquots, with an oil bath at 200 °C for 36 h, and then vacuum transferred to yield **13** (87%) and cyclododecene (**14**, 13%).

Cyclopropylcarbinal (15). Cyclopropylmethyl allyl ether (**11**, 2.5 g, 0.02 mol) and tris(triphenylphosphine)ruthenium dichloride (**1**, 47 mg, 0.25 mol %) were sealed in a Pyrex tube and heated in an oil bath at 200 °C for 48 h. After the products were vacuum transferred, a mixture of 1-propenyl ether **17** (69%) and the title aldehyde **15** (31%) was recovered.

Thermal Fragmentation of 3[*p*-(α-Acetoxyethyl)benzyloxy]-3-methyl-1-butene (6j). The acetoxy ether **6j** (100 mg, 0.38 mmol) was passed dropwise through a heated quartz tube (20 cm long) filled with

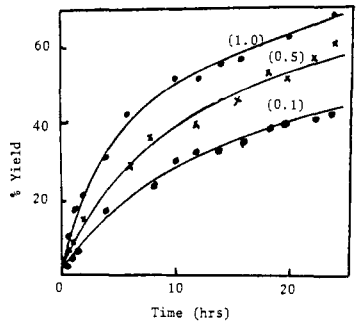


Figure 1.

quartz glass chips with a stream of nitrogen (120 mL/min). The effluent was trapped at −78 °C. Relative yields of the products were determined by GLC and samples isolated by preparative GLC were characterized by ^{1}H NMR. With a reaction temperature of 370 °C a mixture consisting of **6j** (1%), **9j** (74%), and **9k** (25%) was obtained.

***p*-Vinylbenzaldehyde (9k).** ^{1}H NMR δ 5.38 (1 H, dd, J = 1, 10 Hz, vinyl CH), 5.81 (1 H, dd, J = 1, 18.0 Hz, vinyl CH), 6.77 (1 H, dd, J = 10, 18 Hz, vinyl CH), 7.48 (2 H, d, J = 9 Hz, aryl), 7.80 (2 H, d, J = 9 Hz, aryl), 9.92 (1 H, s, CHO).

Anal. (C_9H_8O) C, H.

Deuterium Isotope Effect. A mixture containing 3-benzyloxy-3-methyl-1-butene (**6a**, 20 mL) and α,α-dimethylallyl benzyl ether-α',α'-d_2 (**8**, 20 mL) with hexamethylbenzene as internal NMR standard was heated in the presence of tris(triphenylphosphine)ruthenium dichloride (**1**, 10 mg) at 190 °C in a one-piece 10-mL round-bottom flask with reflux condenser and stopcock for removal of aliquots. After 6 h:

$$\frac{k_H}{k_D} = \frac{\ln [H_0] - \ln [H]}{\ln [D_0] - \ln [D]} = 1.1$$

Deuterium and Protium Crossover During Ruthenium Catalyzed Allylic Rearrangement. α,α-Dideuterioallyl benzyl ether (**7**, 5 μL) and allyl p-methylbenzyl ether (**20**, 50 μL) were placed in a sealed tube with 1 (10 mg) and heated in an oil bath for 2 h at 200 °C. The resulting mixture was analyzed for deuterium exchange by GC/MS (see Table II).

α,α-Dideuterioallyl benzyl ether (**7**, 50 μL) and allyl p-methylbenzyl ether (**20**, 5 μL) were placed in a sealed tube with **1** (10 mg) and heated in an oil bath for 2 h at 200 °C. Again the resulting mixture was analyzed for deuterium exchange by GC/MS (see Table II).

Effect of Para Substituents on Relative Rate of Redox Fragmentation of 3-Benzyloxy-3-methyl-1-butenes. Substituent effect was determined by combining 3-benzyloxy-3-methyl-1-butene, hexadecane (as internal standard), and a para-substituted ether in equal volumes (500 μL). The mixtures were heated in the presence of tris(triphenylphosphine)ruthenium dichloride (**1**, 1 mol %) at 200 °C in a one-piece 10-mL round-bottom flask with reflux condenser and stopcock for removal of aliquots. The aliquots were analyzed by GLC for the appearance of aldehyde and relative rates were calculated according to the equation

$$\frac{k_p}{k_H} = \frac{\ln [p_0] - \ln [p]}{\ln [H_0] - \ln [H]}$$

Results, after 10 h, are listed in Table I.

To check the possibility of the catalyst undergoing a change over the course of the reaction, the catalyst was first "seasoned" on one substrate and the recovered catalyst was used to catalyze the competition reaction. The following results were obtained: 2h, $k_{CO_2CH_3}/k_H$ = 0.95; 4 h, $k_{CO_2CH_3}/k_H$ = 1.00; 7 h, $k_{CO_2CH_3}/k_H$ = 0.89.

Generation and Decomposition of Ruthenium Benzyl Oxide. Sodium hydride (21.4 mg, 0.51 mmol, 57% oil dispersion) was placed in a 50-mL three-neck flask, fitted with mechanical stirrer and addition funnel, and washed with pentane (2 × 10 mL). THF was introduced followed by benzyl alcohol (55.0 mg, 0.51 mmol) in 10 mL of THF. The resulting mixture was boiled under reflux for 1 h. After the mixture had cooled to room temperature, tris(triphenylphosphine)-ruthenium dichloride (**1**, 500 mg, 0.51 mmol) in 20 mL of THF was added portionwise over 30 min and the resulting mixture stirred overnight at room temperature. The mixture was quenched with H_2O (50 mL) and extracted with pentane (3 × 50 mL). The combined organic extracts were washed with 10% HCl (50 mL), saturated $NaHCO_3$ (50 mL), and saturated NaCl (50 mL), and dried ($MgSO_4$). Removal of solvent by rotary evaporation yielded exclusively benzaldehyde (84%): ^{1}H NMR δ 7.25–8.26 (5 H, m, aryl), 10.00 (1 H, s, CHO).

Effect of Catalyst Concentration on Rate of Redox Fragmentation of 3-Benzyloxy-3-methyl-1-butene. In three one-piece 10-mL round-bottom flasks with reflux condenser and stopcock for removal of aliquots were placed 3-benzyloxy-3-methyl-1-butene (2.0 g, 11.34 mmol) with 0.1, 0.5, 1.0 mol % tris(triphenylphosphine)ruthenium dichloride (**1**, 11.14 mg, 0.01 mmol; 55.73 mg, 0.05 mmol; 111.4 mg, 0.10 mmol, respectively) and n-dodecane, as internal standard. The vessels were heated simultaneously in a 200 °C oil bath and aliquots removed over the course of the reaction. Appearance of benzaldehyde was analyzed by GLC (Figure 1).

Ruthenium Catalyzed Transfer Hydrogenation of Isoprene with Benzyl Alcohol. Benzyl alcohol (3.0 g, 27.74 mmol). tris(triphenylphosphine)ruthenium dichloride (**1**, 285 mg, 0.28 mmol, 1.0 mol %), and isoprene (2.8 mL, 27.74 mmol) were boiled under reflux with a 200 °C oil bath in a one-piece flask with reflux condenser and stopcocked gas inlet tube that reached below the surface of the reaction mixture. A toluene bubble trap cooled with a dry ice–acetone bath was connected to the top of the condenser to trap volatile products. After 12 h a light stream of nitrogen was bubbled through the reaction mixture and then through the toluene filled trap to collect the remaining volatile products. Product distribution was analyzed on a 15 ft × 0.125 in. column of 15% FFAP on 80/100 Chromosorb W at 50 °C. Relative retention times: 3-methyl-1-butene (1), 2-methyl-1-butene (1.08), 2-methyl-2-butene (1.12), isoprene (1.33) (see Table III).

Benzaldehyde (2.9 g, 28.24 mmol), benzyl alcohol (0.1 g, 0.92 mmol), 2-methyl-2-butene (3.0 mL, 28.24 mmol), and tris(triphenylphosphine)ruthenium dichloride (**1**, 290 mg, 0.28 mmol, 1.0 mol %) were boiled under reflux with a 200 °C oil bath in the apparatus described above. Volatile components were trapped in toluene at dry ice–acetone temperatures. After 12 h the reaction mixture was swept with a gentle stream of nitrogen to collect the remaining volatile products and the mixture analyzed on a 15 ft × 0.25 in. column filled with 15% FFAP on 80/100 Chromosorb W at 50 °C. No isomeric methylbutenes were detected.

$(Ph_3P)_3RuHCl(CO)$ and $(Ph_3P)_3RuH_2(CO)$ Catalyzed Redox Fragmentation of 6a. 3-Benzyloxy-3-methyl-1-butene (**6a**, 2.0 g, 11.34 mmol) and 112 mg (1 mol %) of dihydridocarbonyltris(triphenylphosphine)ruthenium(II) or 117 mg (1 mol %) of chlorohydridocarbonyltris(triphenylphosphine)ruthenium(II) were heated in the usual vessel for 19 h at 200 °C as described above for **1** as catalyst, yielding benzaldehyde (73 and 74%, respectively).

Acknowledgment is made to the Research Corporation and to the National Science Foundation for support of this research.

References and Notes

(1) For a review of homogeneous catalysis by ruthenium complexes see B. R. James, *Inorg. Chim. Acta*, 73 (1970).
(2) J. Blum and Y. Becker, *Isr. J. Chem.*, **8**, *Suppl., Proc. Isr. Chem. Soc.*, 2p (1970).
(3) J. Blum and Y. Pickholtz, *Isr. J. Chem.*, **7**, 723 (1969).
(4) A detailed description of the ruthenium species involved is unknown. Therefore, the ligands on ruthenium are not shown in the following equations. Ruthenium is assumed to remain in the (II) oxidation state throughout.
(5) This type of reaction was suggested previously for ruthenium(II) alkoxides: Y. Sasson and J. Blum, *J. Chem. Soc., Chem. Commun.*, 309 (1974), and references cited therein.
(6) R. C. Cookson and S. R. Wallis, *J. Chem. Soc. B*, 1245 (1966).
(7) Generation of carbonyl compounds by β-ellmination of ruthenium(II) hydride from a ruthenium(II) alkoxide was recently postulated as a step in the oxidation of alcohols by amine *N*-oxides which is catalyzed by **1**: K. B. Sharpless, K. Akashi, and K. Oshima, *Tetrahedron Lett.*, 2503 (1976).
(8) P. S. Hallman, B. R. Mac Garvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).
(9) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 2947 (1970).
(10) For reviews see D. Lednicer, "Latent Functionality in Organic Synthesis", *Adv. Org. Chem.*, **8**, 179 (1972); D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974); D. Seebach and D. Enders, *Angew. Chem., Int. Ed. Engl.*, **14**, 15 (1975).
(11) Direct, infrared spectroscopic evidence for the in situ generation of a ruthenium hydride from **1** was reported for the reaction of **1** with allylbenzene.[3] In situ generation of ruthenium hydrides by the reaction of **1** with alcohols is also known.[1] For the redox fragmentation of dimethylallyl benzyl

ethers, traces of benzyl alcohol, derived from the ether, may serve as cocatalyst.
(12) P. Taylor and M. Orchin, *J. Am. Chem. Soc.*, **93**, 6504 (1971).
(13) C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **95**, 2240 (1973).
(14) (a) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974); (b) C. A. Bertelo, and J. Schwartz, *ibid.*, **97**, 228 (1975).
(15) (a) J. C. Bailar, Jr., and H. Itatani, *J. Am. Chem. Soc.*, **89**, 1592 (1967); (b) J. C. Bailar, Jr., H. Itatani, M. J. Crespi, and J. Geldard, *Adv. Chem. Ser.*, **No. 62**, 103 (1967); (c) H. A. Tayim and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **89**, 4430 (1967).
(16) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).
(17) R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, **78**, 6084 (1956).

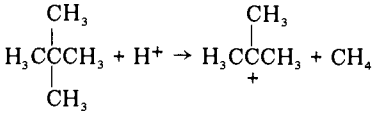
Thermodynamics of Hydrocarbon Oxidations by Superacids

John W. Larsen

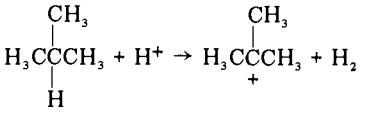
Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916. *Received September 20, 1976*

Abstract: The enthalpies of the various reactions which have been proposed to explain the formation of carbenium ions from alkanes in SbF_5–FSO_3H are calculated. Only those reactions which involve both H^+ and SbF_5 (or FSO_3H) as oxidizing agents have favorable enthalpies. For hydride abstraction from isobutane by H^+ in magic acid, the free energy is estimated to be slightly negative. Oxidations of alkanes by SbF_5 without concomitant reduction of H^+ are not possible. The formation of the *tert*-butyl cation from isobutane in magic acid probably occurs by a varying mixture of two reactions, oxidation by H^+ and oxidation by both H^+ and SbF_5.

In 1964 Brouwer and Mackor first reported the formation of stable cations from alkanes.[1] In 1967 Olah and Lukas published the first of a long series of papers dealing with the formation of stable cations from alkanes by methide or hydride abstraction.[2] While neopentane clearly reacts by protonation to give methane (eq 1), the claim that isobutane reacted by



(1)



(2)

protonation followed by loss of hydrogen (eq 2) was clouded by the observation that the necessary quantity of H_2 was not observed.[3] To explain this, it was suggested that the H_2 reduced one of the components of the acid solution, either FSO_3H or SbF_5.[3] Since that time, four different research groups have contacted H_2 and solutions of SbF_5 in HF or FSO_3H and none have observed any reaction.[4-7] However, the reaction between neat SbF_5 and H_2 (50 atm at room temperature) goes completely to HF and SbF_3.[7] Olah suggests that the reaction is slowed by coordination of SbF_5 in the various solvents.[7] He also suggested that the reduction occurs in systems containing alkanes because "nascent" hydrogen, i.e., the hydrogen emerging from the pronated alkane, is particularly active and capable of reducing SbF_5.[7]

In some systems it has been demonstrated that cations can be formed by oxidation of hydrocarbons by FSO_3H or SO_3 formed from FSO_3H.[6,8] In one of these cases,[6] only easily oxidizable hydrocarbons giving very stable carbenium ions were studied, and their observations may not be relevant to alkanes. However, Bobilliart and co-workers[8] have claimed oxidation of *n*-alkanes by SO_3 in fluorosulfonic acid. Much earlier it was established that hydrogen exchange between alkanes and sulfuric acid occurred by an ionic chain mechanism, the first step of which was oxidation of hydrocarbon to give a carbenium ion and SO_2.[9] Lukas has reported the formation of cations from hydrocarbons in SbF_5 in the absence of FSO_3H (eq 3):[10]

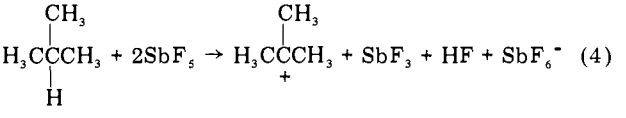
$$2RH + 3SbF_5 \rightarrow 2R^+ + H_2 + SbF_3 + 2SbF_6^- \quad (3)$$

Olah has criticized Lukas' work pointing out that his observations might be due to hydride abstraction by protons present if the system were not kept completely anhydrous.[7]

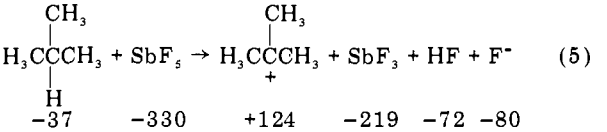
We felt the application of classical thermodynamics to these reactions would yield insight, in the form of establishing which reactions were thermodynamically possible and to identify the driving force for these reactions. Accordingly, we have calculated as best we could the enthalpies of all of the reactions described above. To do this we have had to make a number of approximations and assumptions, some of which are open to just criticism. These calculations are approximate. Our claim is only that *strongly* endothermic reactions will not take place, and strongly exothermic reactions may take place, if the kinetics permit. Fortunately, the results are such that some reactions are obviously impossible, and no conceivable error in our assumptions could make them plausible. It also proved possible to check the most questionable of our assumptions using reliable data.

Oxidation by Antimony Pentafluoride

Equation 4 is best handled as the sum of two reactions, 5 and 6.



(4)



(5)

−37 −330 +124 −219 −72 −80

For this reaction, liquid SbF_5 is the solvent. The number under each molecule or ion is its heat of formation in kilocalories/mole. The heat of formation of liquid isobutane from Stull, Westrum, and Sinke[11] is used, assuming that the heat of solution of isobutane in antimony pentafluoride is 0, an assumption which will not be in error by more than 1 or 2 kcal/mol. The heat of formation of liquid SbF_5 is that reported by