The kinetic data are listed in Tables III-VII.

Acknowledgment. We are grateful to Miss Takako Ishibashi for helpful discussions and experimental assistance.

Registry No. 6a, 539-80-0; **6b**, 3839-48-3; **7**, 17346-16-6; **8a**, 75918-92-2; **8b**, 75933-25-4; **8c**, 75918-93-3; **12**, 75918-94-4; **13**, 75918-95-5; **14**, 75918-96-6; **15**, 75933-26-5; **16**, 75933-32-3; **18**, 75918-97-7; **19b**, 51932-77-5; **20a**, 75918-98-8; **20b**, 75918-99-9; **20c**, 75919-00-5; **20d**, 75919-01-6; **24**, 75919-02-7; **25**, 75919-03-8; 2-phenyltropone, 14562-09-5; cycloheptatriene, 544-25-2; 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer, 38883-84-0; 2,5-dipropyl-3,4-diphenylcyclopentadienone, 61202-93-5; 2,5-dibutyl-3,4-diphenylcyclopentadienone, 75919-04-9; 6-(dimethylamino)fulvene, 696-68-4.

Solvomercuration–Demercuration. 8. Oxymercuration–Demercuration of Methoxy-, Hydroxy-, and Acetoxy-Substituted Alkenes[1]

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Received August 25, 1980

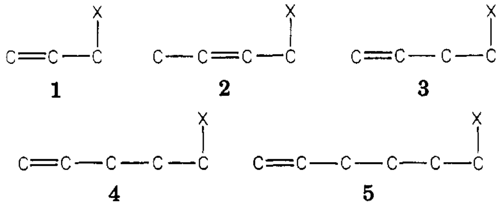
The oxymercuration–demercuration (OM–DM) of a series of methoxy-, hydroxy-, and acetoxy-substituted alkenes was examined. The systems examined were the allyl, crotyl, 3-buten-1-yl, 4-penten-1-yl, and 5-hexen-1-yl. The methoxyalkenes undergo hydration with very high regioselectivity and almost quantitative yield in all cases. However, a small –I effect is observed in the case of the allylalkene (97.1% Markovnikov vs. 99.5% in 1-hexene). Moreover, in the crotyl case, a major directing effect is observed: 97.7% 3-ol, 2.3% 2-ol. The other three alkenes undergo the OM reaction with no effect from the methoxy group (99.5% Markovnikov isomer). In contrast, only allyl-, crotyl-, and 3-buten-1-yl alcohols produce major amounts of hydrated products, the diols. While no hydroxyl group directing effect is observed in the allyl system, a major one is again seen in the case of the crotyl: 93.5% 1,3-diol and 6.5% 1,2-diol. The major products from the 4-penten-1-yl and 5-hexen-1-yl alcohols are 2-methyltetrahydrofuran and 2-methyltetrahydropyran, respectively, resulting from OH-5 and OH-6 neighboring group participation in the OM stage. The acetoxy alkenes undergo hydration to give diols in ca. 80% yield with ca. 20% unreacted starting material. This is the result of a competitive deoxymercuration reaction which is occurring in the DM stage. However, the yield of hydrated products can be increased by varying the amount of base used in the DM. Neighboring-group participation, AcO-5, is observed in the allyl system only, resulting in a 65% yield of the Markovnikov oxymercurial, by ^{1}H NMR analysis, and a 35% yield of the acetoxy-exchanged mercurial. Again, a major –I-directing effect of the acetoxy group was observed in the crotyl system but not in the others. In addition to the expected 1,2- and 1,3-diols, the OM–DM of crotyl acetate also resulted in small amounts of the unexpected 2,3-diol under kinetic conditions. Finally, a modified DM procedure has been developed which is compatible with the acetoxy group.

The oxymercuration–demercuration (OM–DM) of olefins is an extraordinarily valuable method for the Markovnikov hydration of olefins and dienes with remarkably high regioselectivity.[1,3] For example, 1-hexene undergoes reaction to give a 94% yield of alcohols, a 99.5% yield of 2-hexanol and a 0.5% yield of 1-hexanol (eq 1).

$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow[\text{THF, } H_2O]{Hg(OAc)_2} \xrightarrow[\text{2. NaBH}_4]{\text{1. NaOH}} CH_3(CH_2)_3C(OH)HCH_3 \quad (1)$$

While there are numerous examples in the literature on the OM–DM of functionally substituted alkenes, there are but a few detailed, systematic studies.[4-10] Consequently, we undertook such a study on representative functionally substituted acyclic alkenes. The results are detailed and discussed in this as well as the following paper in this series.

Chart I[a]



[a] X = OCH$_3$, OH, OAc.

Results and Discussion

The alkene systems examined were the allyl (**1**), crotyl (**2**; 2-buten-1-yl), 3-buten-1-yl (**3**), 4-penten-1-yl (**4**), and 5-hexen-1-yl (**5**) with the methoxy, hydroxy, and acetoxy functional groups (Chart I).

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(1) The oxymercuration–demercuration of unsaturated alcohols was discussed earlier in connection with a study of the reaction of dienes: H. C. Brown, P. J. Geoghegan, Jr., J. T. Kurek, and G. J. Lynch, *Organomet. Chem. Synth.*, 1, 7 (1970).

(2) Texaco research fellow at Purdue University, 1972–1973. Graduate research assistant, 1969–1972, on a study supported by a grant from the Esso Research and Engineering Co.

(3) H. C. Brown and P. J. Geoghegan, Jr., *J. Org. Chem.*, **35**, 1844 (1970).

(4) J. L. Jernow, D. Gray, and W. D. Closson, *J. Org. Chem.* **36**, 3511 (1971).

(5) M. Barelle and M. Apparu, *Bull. Soc. Chim. Fr.*, 2016 (1972).

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(8) F. D. Gunstone and P. R. Inglis, *Chem. Phys. Lipids*, **10**, 73, 89, 105 (1973).

(9) Much of the earlier work on the oxymercuration stage has been reviewed; see ref 10.

(10) W. Kitching, *Organomet. Chem. Rev.*, **3**, 61 (1968).

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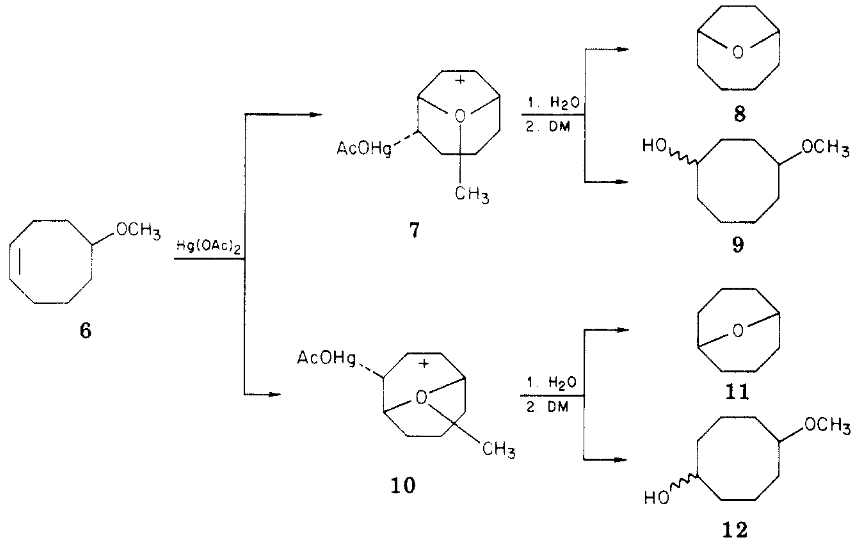
Table I. Oxymercuration-Demercuration of Methoxy Substituted Olefins

R of ROMe	t_1,[a] s	t_2,[b] min	% yield[c] of methoxy alcohols	product distribution: product	%[c]
allyl[f]	10	30	94	1-methoxy-2-propanol	97.1
				1-methoxy-3-propanol	2.9
3-buten-1-yl	14	30	97	4-methoxy-2-butanol	99.1
				4-methoxy-1-butanol	0.9
crotyl	35	30	100	4-methoxy-2-butanol	97.7
				1-methoxy-2-butanol	2.3
4-penten-1-yl[g]	15	30	95[d]	5-methoxy-2-pentanol	99.8
				5-methoxy-1-pentanol	0.2
5-hexen-1-yl[h]	12	30	93[e]	6-methoxy-2-hexanol	99.8
				6-methoxy-1-hexanol	0.2

[a] Time for the yellow color to disappear. [b] Complete time for OM stage. [c] By VPC analysis. [d] Small amounts of residual olefinic ether was observed in the product but was not quantitatively analyzed. [e] 6% of residual 6-methoxy-1-hexene was present in the product. [f] No 2-methoxy-1-propanol could be detected in the product. [g] No 4-methoxy-1-pentanol or 2-methyltetrahydrofuran could be detected in the product. [h] No 5-methoxy-1-hexanol or 2-methyltetrahydropyran could be detected in the product.

Scheme I



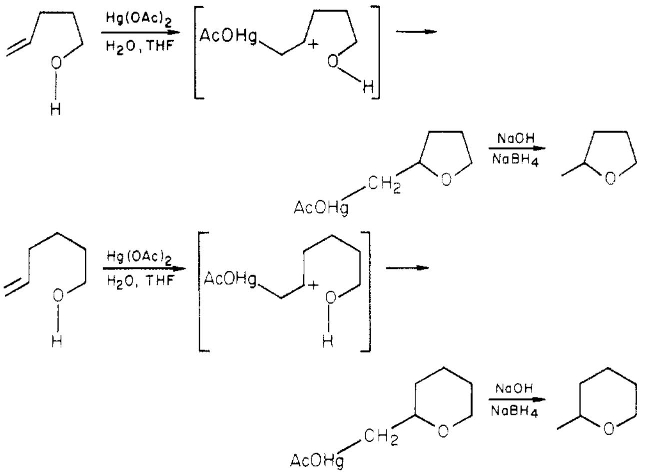
Methoxy-Substituted Alkenes. These alkenes undergo hydration in all cases in nearly quantitative yield and with very high regioselectivity. The only products observed are the methoxy alcohols. The results are summarized in Table I.

The allylalkene undergoes hydration with very high Markovnikov regioselectivity, 97.1%. Nevertheless, it is lower than that observed for a typical monosubstituted olefin such as 1-hexene. This is readily attributable to the –I effect of the methoxy group. However, in the case of crotyl, where both carbon atoms are substituted, a major directing effect is observed. Gunstone and Inglis[8] have also observed a similar directing effect in the OM–DM of several methoxy-substituted, unsaturated, fatty acid esters.

It is also significant that no evidence of neighboring-group participation by the methoxy group was observed. Moreover, in a study on the methoxymercuration–demercuration of 4-penten-1-yl and 5-hexen-1-yl methyl ethers by Pritzkow and co-workers,[11] a similar conclusion was reached. On the other hand, Closson and co-workers[4] have reported that the OM–DM of 5-methoxycyclooctene (6) gives two bicyclic ethers (8 and 11), apparently arising from neighboring-group participation (Scheme I).

Consequently, the OM–DM of 6 was reinvestigated. No products arising from neighboring-group participation (i.e., 8 and 11) could be detected, however. The only products observed appeared to be methoxycyclooctanols.[12]

Scheme II



Hydroxy-Substituted Alkenes. The results of the OM–DM of these alkenes are summarized in Table II. High yields of the hydrated products, the diols, are obtained from the allyl, crotyl, and 3-buten-1-yl alkenes. In

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(11) V. B. Beyer, C. Duschek, H. J. Franz, R. Hahn, W. Hobold, P. Kluge, W. Pritzkow, and H. Schmidt, *J. Prakt. Chem.*, 312, 622 (1970).

(12) These compounds are identified on the basis of VPC retention times.

Table II. Oxymercuration–Demercuration of Unsaturated Alcohols

R of ROH	t_1,[a] s	t_2,[b] min	% yield[c,d]	product distribution: product	% [c]
allyl	3	30	75 (97)	1,2-propanediol	99.0[e]
				1,3-propanediol	1.0[e]
3-buten-1-yl	6	30	87 (93)	1,3-butanediol	99.2
				1,4-butanediol	0.7
				tetrahydrofuran	0.1[f]
crotyl	12	30	84 (93)	1,3-butanediol	93.5
				1,2-butanediol	6.5
4-penten-1-yl	5	30	95	2-methyltetrahydrofuran	99.4
				1,4-pentanediol	0.6
				1,5-pentanediol	trace
5-hexen-1-yl	7	30	100	2-methyltetrahydropyran	91.9
				1,5-hexanediol	8.1
				1,6-hexanediol	trace

[a-c] See corresponding footnotes in Table I. [d] Total VPC yield of all products listed. Numbers in parentheses are based on a continuous extraction procedure for diol product isolation. Numbers not enclosed in parentheses refer to a multiple simple extraction procedure. [e] These isomer distributions have been corrected for the fact that the efficiency of recovery of the 1,3-propanediol diacetate from a blank OM–DM is only 0.6 of that for the 1,2-propanediol diacetate. [f] Determined from a run made in pure water with no THF solvent.

Table III. Oxymercuration–Demercuration of Acetoxy-Substituted Olefins

R of ROAc	t_1,[a] s	t_2,[b] min	reduction conditions[c]	% yield: residual unsaturated alcohols[d]	% yield: diols[d,e]	diol distribution, %: 1,2	1,3	2,3	1,4	1,5
allyl	30	30	normal	14	(80)	99.2[f]	0.8[f]			
		60	normal	18	(77)					
		30	4.5 M NaOH	1	(92)					
		30	4.5 M NaOH	1	62	99.2[f]	0.8[f]			
3-buten-1-yl	14	30	normal	28	64		98.8		1.2	
		30	4.5 M NaOH	6	82		99.0		1.0	
crotyl	90	30	normal	12[g] + 6[h]	77	6.7	91.9	1.4		
		30	4.5 M NaOH	6[g] + 1[h]	89	5.6	92.9	1.5		
4-penten-1-yl	15	30	normal	16–18	67–80				100[l]	
		30	4.5 M NaOH	8	60–70				100	
		30	4.5 M NaOH + 30 min of stirring[i]	8	67–70				100	
		30	4.5 M NaOH + 30 min of reflux[j]	4	90				100	
		30	no NaOH[k]	5	89				100	
5-hexen-1-yl	24	30	normal	5	87					100[m]

[a,b] See corresponding footnotes in Table II. [c] Normal refers to the standard procedure, whereas, 4.5 M NaOH refers to the the substitution of 4.5 M NaOH for the 3.0 M NaOH in the reduction stage of the standard procedure. [d] By VPC analysis. [e] Total VPC yield of diols. Numbers in parentheses are based on a continuous extraction procedure for diol product extraction. Numbers not in parentheses refer to a multiple simple extraction procedure. [f] Corrected for relative recovery efficiencies. [g] Crotyl alcohol. [h] 3-Buten-2-ol. [i] 4.5 M NaOH was used in the reduction stage and the reaction solution stirred for 30 min after the 4.5 M NaOH had been added, before addition of the $NaBH_4$ solution. [j] 4.5 M NaOH was used in the reduction stage and the reaction solution refluxed for 30 min after the 4.5 M NaOH had been added, before addition of the $NaBH_4$ solution. [k] No NaOH solution was used to initiate the reduction stage; the $NaBH_4$ solution was added directly. [l] No (<3%) 2-methyltetrahydrofuran could be detected in the product. [m] No (<3%) 2-methyltetrahydropyran could be detected in the product.

this case, no hydroxyl group directing effect is seen in the allyl system. However, a major effect is again observed in the crotyl system.

In contrast, the major products from 4-penten-1-ol and 5-hexen-1-ol are the cyclic ethers, resulting from neighboring-group participation by the hydroxyl group (Scheme II).

Previous studies have demonstrated a remarkable OM rate enhancement as a result of this participation.[13] Furthermore, the synthetic utility of this phenomenon has been recently demonstrated.[14-18]

Acetoxy-Substituted Alkenes. Because of the ease with which the acetate group is hydrolyzed during the DM stage, the products from the OM–DM of these substrates were analyzed as the diols. The results are summarized in Table III.

Surprisingly, the yields of hydrated products from the acetoxy-substituted alkenes, with the exception of 5-hexen-1-yl, are low, ca. 80%. Moreover, the remainder of the material is essentially the hydrolyzed alkene. However, ^1H NMR analysis of the OM reaction mixtures failed to reveal any starting alkene. These observations led us to suspect that a concurrent deoxymercuration was occurring during the DM stage. Since deoxymercurations are strongly dependent on pH,[19] it appeared desirable to test this possibility. Indeed, by employment of a more con-

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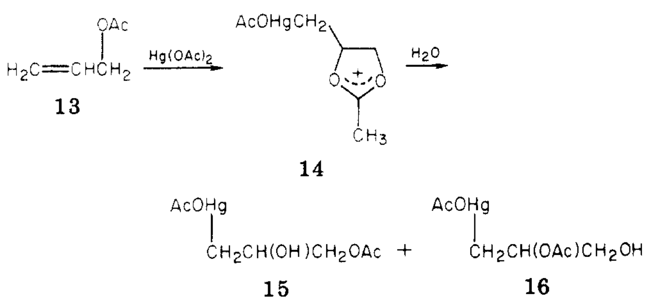
(13) J. Halpern and H. B. Tinker, *J. Am. Chem. Soc.*, **89**, 6427 (1967).
(14) C. Ganter, *Top. Curr. Chem.*, **67**, 15 (1976).
(15) D. P. G. Harmon, G. F. Taylor, and R. N. Young, *Aust. J. Chem.*, **30**, 589 (1977).
(16) E. J. Corey, G. E. Keck, and I. Szekely, *J. Am. Chem. Soc.*, **99**, 2006 (1977).
(17) L. Overman, *J. Chem. Soc., Chem. Commun.*, 1196 (1972).
(18) L. Overman and C. B. Campbell, *J. Org. Chem.*, **39**, 1474 (1974).
(19) F. G. Bordwell and M. L. Douglass, *J. Am. Chem. Soc.*, **88**, 993 (1966).

Scheme III



centrated solution of base, 4.5 M sodium hydroxide as compared to the 3 M solution used under standard conditions, the yield of hydrated products increased significantly with a corresponding decrease in the yield of hydrolyzed starting material. Evidently, deoxymercurations are quite facile in the OM–DM of these acetoxyalkenes.

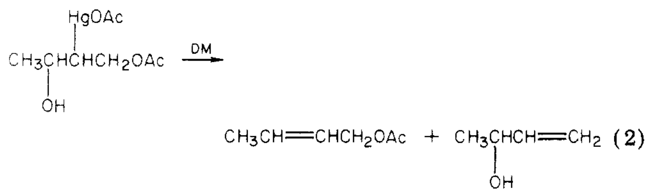
The case of 4-penten-1-yl acetate was of particular interest. In contrast to the other systems, the initial results obtained here were unreproducible, and often poor material balances were observed. It was discovered that only when the amount of time between the addition of the sodium hydroxide and the addition of the sodium borohydride is controlled, reproducible results are obtained. Furthermore, it appears that excellent yields of hydrated product can be obtained by merely carrying out the DM without the prior addition of base. On the other hand, once the base is added, the intermediate which results must be further hydrolyzed (and apparently with great difficulty) in order to obtain a quantitative demercuration. However, we did not investigate the nature of these intermediates.

The possibility of neighboring-group participation was also investigated. However, since we were forced to analyze the OM–DM products as the diols, it was decided to examine the OM reaction mixtures by using ^{1}H NMR analysis.

In the case of allyl acetate (**13**), two oxymercurials are formed in detectable amounts—the Markovnikov mercurial (**15**) in 65% yield and the acetoxy-exchanged mercurial (**16**) in 35% yield. This strongly suggests the intermediacy of acetoxonium ion (**14**, Scheme III).

While AcO-5 participation is apparent in the case of allyl acetate, the corresponding AcO-6 participation which is possible in the OM–DM of both crotyl and 3-buten-1-yl acetate was not detected.

However, the OM–DM of crotyl acetate did exhibit one unusual result. Surprisingly, in addition to the expected 1,2- and 1,3-diols, a small amount of the 2,3-diol is observed as well. Moreover, the yield of the 2,3-diol increases markedly with time at the expense of the 1,3-diol (Table IV). Furthermore, a careful analysis of the hydrolyzed starting material revealed not only crotyl alcohol but also methyl vinyl carbinol as well. Evidently deoxymercuration is occurring in both possible directions (eq 2).



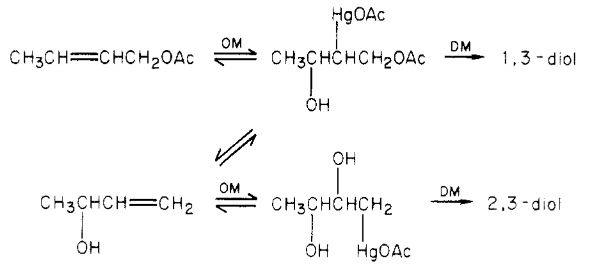
It is well-known that the oxymercuration reaction is reversible. Clearly, in the case of the crotyl system, the reverse reaction can occur in both directions to regenerate the starting material as well as methyl vinyl carbinol. A subsequent OM–DM on this species will then result in the 2,3-butanediol (Scheme IV).

Table IV. Oxymercuration–Demercuration of Crotyl Acetate as a Function of Time[a]

	product distribution,[c] %				
	butanediols				
t_2[b]	1,3	1,2	2,3	crotyl alcohol	1-buten-3-ol
30 min	71	5	1	12	6
1 h	68	6	3	11	7
2 h	69	5	4	8	6
4 h	58	4	14	13	7
24 h	29	5	45	5	6

[a] Standard reduction conditions. [b] Complete reaction time for the oxymercuration stage before the addition of 3.0 M NaOH solution. [c] By VPC analysis.

Scheme IV



As stated previously, the acetate group is not very tolerant to the standard DM conditions. Consequently, we explored several modified DM procedures with the hope of developing one which is useful for synthetic purposes. We examined the OM–DM of 1-hexene in which less basic DM procedures were employed. The best results were obtained by using 2 equiv of cold sodium hydroxide followed by the dropwise addition of a cold, freshly prepared, aqueous solution of sodium borohydride, all at 0 °C and with diethyl ether as a cosolvent. Indeed, with this modified procedure, 4-penten-1-yl acetate could be converted to 4-hydroxypent-1-yl acetate in 73% isolated yield.

Conclusion

The oxymercuration–demercuration of methoxy alkenes results in high yields (>90%) of methoxy alcohols. The methoxy group exhibits only a small -I effect in the case of allyl and a major effect in the case of crotyl.

Similarly, excellent yields of diols are obtained from the OM–DM of hydroxy olefins except when OH-5 and OH-6 participation is possible. In these cases, the major products are the cyclic ethers. The hydroxyl group exerts no significant directing effect in the case of allylalcohol, but again, a major effect is observed in the case of crotyl alcohol.

In contrast, the products obtained from the OM–DM of alkenyl acetates under standard conditions are diols. However, the yields are significantly lower because of a competitive deoxymercuration during the DM stage. Increasing the amount of base used in the DM, in most cases, results in major increases in the yield of hydrated products.

Neighboring-group participation by the acetoxy group is observed only in the case of allyl (AcO-5).

Finally, a less basic DM procedure has been developed to allow for the survival of the acetate group.

Experimental Section

Materials. All of the unsaturated alcohols used were commercially available and were distilled prior to use: allyl alcohol (Fisher), 3-buten-1-ol (Columbia), 2-buten-1-ol (Aldrich), 4-penten-1-ol (Columbia), and 5-hexen-1-ol (Chemical Samples). The unsaturated acetates used were prepared by the acetylation of the corresponding alcohol with acetic anhydride and a catalytic amount of dry pyridine by the method described below except for crotyl acetate (Columbia) and in part 4-penten-1-yl acetate (Chemical Samples) which were commercially available. Samples of the olefinic methyl ethers listed in Table I were prepared from the corresponding alcohol by conversion to the sodium alkoxide and subsequent alkylation with methyl iodide and are described below. The 5-methoxycyclooctene was prepared as described below by the monomethoxymercuration of 1,5-cyclooctadiene using the general methoxymercuration–demercuration procedure of Brown and Rei.[20] Mercuric acetate (Baker or Mallinckrodt Analytical Reagent) and tetrahydrofuran (THF, Quaker Oats Co.) were commercially available and used as obtained. The 1-hexene (Aldrich) used was distilled from $LiAlH_4$ prior to use; 2-hexanol was available from Chemical Samples. The starting materials and the authentic samples prepared were characterized by IR and NMR spectral characteristics.

General Procedure for the Preparation of Acetates from Alcohols. The alcohol (200 mmol) was heated at reflux with 30 mL (ca. 300 mmol) of acetic anhydride and 0.5 mL of dry pyridine for 4 h under the protection of a $CaCl_2$ drying tube. After cooling to room temperature, the solution was poured into 300 mL of water and stirred vigorously for approximately 30 min. Pentane (50 mL) was added, and the layers were separated. The aqueous layer was extracted with two 50-mL portions of pentane. The combined pentane extracts were washed twice with 30-mL portions of saturated $NaHCO_3$ solution and then dried over $MgSO_4$. The solution was filtered, concentrated, and distilled. The following acetates were prepared by this method or slight alterations thereof with a VPC purity on Carbowax 20M of >99% in all cases:

Allyl acetate: bp 101–102 °C; n^{20}_{D} 1.4043 [lit.[21] bp 104 °C (773 mm); n^{20}_{D} 1.4040].

3-Buten-1-yl acetate, bp 43–44 °C (30 mm); n^{20}_{D} 1.4098 [lit.[22] bp 58–59 °C (60 mm); n^{20}_{D} 1.4118].

4-Penten-1-yl acetate: bp 148 °C; n^{20}_{D} 1.4185 (lit.[23] bp 149–150 °C; n^{20}_{D} 1.4162).

5-Hexen-1-yl acetate: bp 82 °C (31 mm); n^{20}_{D} 1.4235 [lit.[24] bp 69 °C (16 mm); n^{21}_{D} 1.4245].

3-Methoxy-1-propene. A nominal 59% NaH dispersion (9.5 g, 229 mmol) was washed with three 40-mL portions of distilled pentane. After the last washing was decanted (under a N_2 flow), the remainder of the pentane was removed by applying a 12-mm water aspirator vacuum. To this was added 150 mL of dimethyl sulfoxide which had been dried over 4-Å molecular sieves and the sodium methylsulfinylmethide generated[25] by heating the mixture under N_2 at 65–70 °C until the evolution of gas almost stopped (ca. 1.5–2.0 h). After the mixture cooled to room temperature, a few milligrams of triphenylmethane was added as an indicator when the solution became bright red. Allyl alcohol was then added dropwise via syringe until the red color was just discharged, which required 9.0 mL (132 mmol) of allyl alcohol. The flask was surrounded by a water bath maintained at 20 °C, and then 8.3 mL (132 mmol) of methyl iodide was added. After the mixture was stirred at room temperature overnight, the flask was equipped with a simple distillation head and the product distilled into a dry ice–acetone cooled receiver by gradually lowering the pressure to 12 mm and then gradually heating the pot to 50 °C to give 8.86 g (123 mmol, 93%) of 3-methoxy-1-propene, n^{20}_{D} 1.3795 (lit.[26] n^{25}_{D} 1.3759).

1-Methoxy-2-butene. A procedure identical with that used for 3-methoxy-1-propene was used to give a mixture of cis and trans isomers: bp 77 °C; n^{20}_{D} 1.3990 [lit.[27] (for the trans isomer) bp 76–77 °C; n^{20}_{D} 1.3990].

4-Methoxy-1-butene. To 100 mL of diglyme which had been dried over 4-Å molecular sieves was added 9.3 g of nominal 58.6% NaH dispersion (227 mmol) followed by 15.2 g (200 mmol) of 3-buten-1-ol (Columbia). The solution was stirred under N_2 until the evolution of gas ceased, and after the mixture cooled somewhat, there was added dropwise 12.45 mL (200 mmol) of methyl iodide. After the mixture stirred overnight at room temperature, the product was distilled out into a dry ice–acetone-cooled receiver in a manner identical with that above. The distillate thus obtained was redistilled to give 13.5 g of fractions boiling from 61–79 °C. The fractions were combined, $LiAlH_4$ added, and the mixture distilled to give 4-methoxy-1-butene: bp 68–70 °C; n^{20}_{D} 1.3902 (lit.[27] bp 68–69 °C; n^{25}_{D} 1.3886). VPC analysis on DC-710 and Carbowax 20M columns indicated the presence of a single impurity (7%, longer retention time) which was shown to be 1,2-dimethoxyethane by mixed injection and NMR spiking analysis.

5-Methoxy-1-pentene. To ca. 100 mL of diethyl ether which had been distilled over benzophenone ketyl was added 10.0 g of nominal 58.6% NaH dispersion (240 mmol) followed by 20.0 mL (16.7 g, 194 mmol) of 4-penten-1-ol under N_2. The solution was stirred 40 h at room temperature and then heated at reflux for 6 h. After the mixture cooled, 15 mL (240 mmol) of methyl iodide was added and the solution heated at reflux for ca. 60 h. At the 30-h point, an additional 2 mL of methyl iodide was added. The reaction was hydrolyzed with 25 mL of water, the layers were separated, the aqueous phase was extracted once with ether, and the combined extracts were dried over K_2CO_3. Filtration followed by distillation gave 9.2 g (41%) of the center-cut fraction of 5-methoxy-1-pentene: bp 96–98 °C; n^{20}_{D} 1.4016 [lit.[28] bp 96–98 °C (764 mm); n^{17}_{D} 1.4032]. The 5-methoxy-1-pentene was flash distilled from $LiAlH_4$ prior to use to assure the absence of 4-penten-1-ol.

6-Methoxy-1-hexene. To ca. 100 mL of triglyme under N_2 which had been distilled from NaH under reduced pressure was added 11.9 g of nominal 58% NaH dispersion (288 mmol) and 24 mL (20 g, 200 mmol) of 5-hexen-1-ol. The mixture was stirred vigorously at room temperature for 2 h and then heated at 80–100 °C for 1 h. At the end of this time, gas evolution had ceased. The solution was brought to room temperature and cooled with an ice–water bath, and 20 mL (320 mmol) of methyl iodide was added dropwise. After the mixture was stirred overnight, VPC examination of a hydrolyzed aliquot indicated no residual 5-hexen-1-ol. Consequently, the flask was fitted with a distilling head and the product distilled into a dry ice–acetone-cooled receiver by reducing the pressure to 12 mm and then gradually heating the pot to 100 °C. The distillate was fractioned to give 18.9 g of pure (VPC, DC-710) 6-methoxy-1-hexene: bp 122 °C; n^{20}_{D} 1.4108 (lit.[29] bp 123 °C; n^{20}_{D} 1.4109).

5-Methoxycyclooctene. The general procedure of Brown and Rei was followed.[20] Thus, to 21.8 g (200 mmol) of 1,5-cyclooctadiene which had been distilled from $LiAlH_4$ under vacuum prior to use was added 200 mL of absolute methanol. To the stirred solution was added 63.7 g (200 mmol) of mercuric acetate. The solution was stirred for 1 h at room temperature and then 200 mL of 3 M NaOH solution was added followed by the dropwise addition of 200 mL of 0.5 M $NaBH_4$ in 3 M NaOH solution. The mixture was stirred until the mercury coagulated (ca. 2 h), 200 mL of distilled pentane was added, and the layers were separated. The aqueous layer was extracted with an additional 200 mL of distilled pentane, and the combined pentane extracts were washed once with 100 mL of water and then dried over K_2CO_3. The mixture was filtered, concentrated on a rotary evaporator, and distilled through a short Vigreux column to give 16.6 g (60%) of 95.0% (VPC, DC-710) pure 5-methoxycyclooctene: bp 85–86 °C (27 mm); n^{20}_{D} 1.4702 [lit.[4] bp 77 °C (26 mm)]. By VPC (DC-710) the material was found to contain 1.2% of residual 1,5-cyclooctadiene and 3.5% and 0.3% of two unidentified impurities of retention times similar but slightly shorter than that of 5-methoxycyclooctene. The 5-methoxycyclooctene was stirred over $LiAlH_4$ overnight and then distilled under reduced pressure, followed by purification by preparative VPC (7 ft × 0.75 in. column of TCEPE on 45/60 Chromosorb W) to give 5-methoxycyclooctene

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(25) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. I, Wiley, New York, 1967, p 310.

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of 99.5% purity and containing no (<0.1%) 1,5-cyclooctadiene but still containing 0.5% of the unidentified impurities previously mentioned above. An NMR spectrum of this purified material was identical with that reported.

Standard Analytical Oxymercuration–Demercuration Procedure. In a 50-mL, round-bottomed flask equipped with a Teflon-covered magnetic stirring bar was placed 1.60 g (5.0 mmol) of mercuric acetate. To this was added 5.0 mL of water, and the mixture was stirred until the salt dissolved to produce a clear solution. Then 5.0 mL of THF was added to produce a yellow precipitate. To the vigorously stirred suspension was added 5.0 mmol of the olefinic compound, and the flask was stoppered. The time needed for the yellow color to disappear was recorded as t_1. The reaction mixture was stirred for an appropriate time, t_2. Then 5.0 mL of 3.0 M NaOH solution was added all at once followed by 5.0 mL of 0.5 M $NaBH_4$ in 3.0 M NaOH all at once with vigorous stirring. After the mixture was stirred until most of the mercury had coagulated (usually 0.5 h), a suitable VPC standard was added and the aqueous phase saturated with K_2CO_3. The upper layer was separated, the aqueous phase was extracted usually with two 5-mL portions of THF or ether, and the combined extracts were dried over K_2CO_3. This was followed by VPC analysis. If an unsaturated acetate was the olefinic substrate, the solution was refluxed for 30 min to 1 h or was allowed to stir at room temperature for several hours before the remainder of the workup was completed.

Modification of the Standard Analytical Oxymercuration–Demercuration Procedure for Continuous Liquid–Liquid Extraction. A liquid–liquid extraction unit was made by a simple modification of a standard Soxhlet extractor. The central chamber was fitted with a glass test tube of slightly smaller diameter, and a long tube 6–8 mm in diameter with one end flared out to make a funnel mouth was placed inside this tube and led up to the condenser drip tip.

In cases where continuous liquid–liquid extraction was employed, the same general OM–DM procedure as described above was followed except that after the aqueous phase was saturated with K_2CO_3, the entire mixture was transferred to the test tube inside of the Soxhlet. Approximately 20 mL of THF was used to wash the reaction flask into the apparatus, and 30 mL of THF was charged to the pot of the extraction apparatus. Extraction was then started, and samples were withdrawn from the pot at various times to analyze for product yield.

VPC Analyses. Two chromatographs were employed: a Hewlett Packard Model 5750 gas chromatograph equipped with a thermal-conductivity detector and using 0.25-in. columns and a Varian Model 1200 gas chromatograph equipped with a flame-ionization detector and using 0.125-in. columns, both equipped with disk chart integrators. Stainless-steel columns were used throughout with Chromosorb W, AW/DMCS, and Varaport-30 supports. Standard liquid phases of DC-710, SE-30, and Carbowax 20M (the latter with a small amount, ca. 0.5%, of Armac 18D) were used for product analyses and routine purity checks. Isomeric products from OM–DM runs were analyzed on Carbowax 20M. Product yields determined in this manner are estimated to be good to within ±3%. In the analysis of isomers from an OM–DM reaction, e.g., the Markovnikov and anti-Markovnikov isomers, it was assumed that the isomers have identical thermal-conductivity and flame-ionization response factors. In the isomer distributions reported in the text to 0.1%, the estimated uncertainty in the value is at least 0.2% for percentages in the 1% range and somewhat larger for larger percentages. Unless otherwise noted, isomer peaks were identified by mixed injection of the reaction mixture with approximately an equal amount of the compound in question. In all cases, a corresponding increase in the size of the peak was observed with no evidence of splitting or shouldering.

Identification and Analyses of Products from the OM–DM of Unsaturated Alcohols and Acetates. Since diol peaks are usually distorted for low molecular weight diols, yield analyses were accomplished by the Tri-Sil method described below, and isomer distributions were determined by either the Tri-Sil or diacetate method described below. The actual method used depended on the unsaturated substrate. Thus, for allyl alcohol, crotyl alcohol, and their corresponding acetates the diacetate method was employed. For 3-buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, and their acetates, the Tri-Sil method was employed.

In the analysis for the 1,3- and 1,2-propanediols from OM–DM of allyl alcohol or acetate the numbers reported in the text were corrected for the fact that the efficiency of recovery of the 1,3-diacetoxypropane was only 0.6 of that for the 1,2-diacetoxypropane. The correction factor of 0.6 was determined by carrying out a blank OM–DM run with no unsaturated substrate present and adding 2.5 mmol of each diol in a 5.0-mmol scale run.

In the analysis for the 1,3- and 1,4-butanediols arising from the OM–DM of 3-buten-1-ol and its acetate, a complication in the Tri-Sil method of analysis existed in that Tri-Sil itself had a peak which was identical in retention time (established by mixed injection) with the bis(trimethylsilyl) ether of 1,4-butanediol. In order to correct for this, we made a blank OM–DM run with no unsaturated substrate added and treated it exactly the same as for the OM–DM reaction. The area of the peak in this blank run for the 1,4-diol derivative was then subtracted out from that of the OM–DM reaction. The area subtracted out was approximately 15% of the total area observed for the peak.

A large majority of products arising from the OM–DM of unsaturated alcohols and acetates were commercially available and were distilled prior to use: 1,2-propanediol (Matheson Coleman and Bell), 1,3-butanediol (Eastman), 1,4-butanediol (Eastman), 2,3-butanediol (Fulka), 1,5-pentanediol (Matheson Coleman and Bell), 1,6-hexanediol (K and K). A sample of 1,2-butanediol was available from a previous study. A sample of 1,4-pentanediol was prepared by the $LiAlH_4$ reduction of levulinic acid. A pure sample of 1,5-hexanediol was available from the preparative OM–DM of 5-hexen-1-yl acetate followed by saponification prepared in the course of another study.[30] Both 2-methyltetrahydrofuran (Quaker Oats Co.) and 2-methyltetrahydropyran (Aldrich) were commercially available and were distilled prior to use.

Diol VPC Analysis by the Tri-Sil Method. In a 1-dram vial was placed 0.25 mL of the dried reaction solution containing the diol, and 0.25 mL of Tri-Sil (Pierce Chemical Co.) was added. The vial was immediately stoppered, and the contents were agitated by shaking. After ca. 10 min, the solution was centrifuged to pack the finely divided solid (amine hydrochloride salts). The resulting supernatant liquid containing the bis(trimethylsilyl) ethers was then analyzed by VPC on either SE-30 or DC-710 columns.

Diol VPC Analysis by the Diacetate Method. The dried THF extract from the OM–DM was concentrated on the rotary evaporator. For a 10-mmol OM–DM run, the residue was treated with 10 mL of acetic anhydride and 50 μL of dry pyridine. The mixture was stirred and heated at reflux for 3–4 h, cooled, and hydrolyzed by being stirred vigorously with 10 mL of water for 30 min to 1 h, and the product was finally extracted with four 10-mL portions of pentane. The combined pentane extracts were washed with one-third their volume of saturated $NaHCO_3$ solution and then dried over $MgSO_4$. The resulting solution was then analyzed by VPC, usually on a Carbowax 20M column.

Preparative OM–DM of 4-Penten-1-yl Acetate with a Modified, Less Basic Reduction Procedure. Isolation of 5-Acetoxy-2-pentanol. Into a 250-mL, round-bottomed flask fitted with a Teflon-covered magnetic stirring bar were placed 8.00 g (25 mmol) of mercuric acetate and 25 mL of water. After the mixture was stirred until the salt dissolved, 25 mL of THF was added followed by 3.60 mL (3.23 g, 25 mmol) of 4-penten-1-yl acetate via syringe. The solution was stirred for 30 min at room temperature. Then 25 mL of diethyl ether was added, and the contents were cooled to 0 °C with an ice–water bath, followed by a dropwise addition of 16.7 mL of cold 3.0 M NaOH over a ca. 5-min period. Then 25 mL of freshly prepared cold 0.5 M $NaBH_4$ in water solution was added dropwise and with vigorous stirring. The $NaBH_4$ solution was added at such a rate as to keep the temperature below 6 °C. After all of the hydride solution had been added, 20 g of NaCl was added, the solution was stirred for ca. 5 min, the contents were transferred to a separatory funnel, and the layers were separated as quickly as possible. The aqueous phase was quickly extracted with portions of ether (2 × 25 mL), and the combined extracts were dried first over Na_2SO_4 and then over $MgSO_4$. The solution was filtered, concentrated on the rotary

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(30) P. Burke, Ph.D. Thesis, Purdue University, 1973, p 239.

evaporator, and then evaporatively distilled by molecular distillation at 2 μm by using a heat gun very carefully to gently warm the pot and distillation head to give 2.66 g (73%) of product in a four-fingered collector. The largest fraction which consisted of ca. 80–85% of the total material distilled was 95–96% pure on DC-710 and Carbowax 20M columns. A 2–3% impurity had a shorter retention time than the major peak on the Carbowax 20M column but a longer retention time on DC-710 and consequently was assumed to be the corresponding diacetate, i.e., 1,4-diacetoxypentane. There was present no detectable amount (<0.2%) of 1,4-pentanediol. The remaining, ca. 15%, distilled material was of a combined purity of ca. 93% and contained larger amounts of the diacetate peak in addition to small amounts of 4-penten-1-ol and its acetate. Physical and spectral characteristics on the major fraction were as follows: $n^{20}D$ 1.4320 (lit.[31] n^{20}_D 1.4314); IR (neat) 2.92, 5.77, 8.0, 9.6 μm; NMR (CCl_4) δ 1.15 (d, J = 6 Hz, 3), 1.3–1.9 (m, 4), 2.00 (s, 3), 3.65 (s, OH by D_2O exchange, 1), 3.77 (sextet, J = 6 Hz) overlapping 4.03 (t, J = 6 Hz) for a 3-H total.

Identification and Analyses of Products from the OM–DM of Unsaturated Methyl Ethers. For analyses of 2-methyltetrahydrofuran and 2-methyltetrahydropyran at the 0.1% level, it was necessary to use a 2-ft Poropak Q column to get adequate resolution from the THF solvent.

Samples of 1-methoxy-2-propanol (Chemical Samples) and 3-methoxy-1-propanol (Sapon) were available. The interchanged product, 2-methoxy-1-propanol, was prepared by the methoxymercuration–demercuration of allyl alcohol by using the conditions of the general procedure described:[20] bp 127–130 °C (lit.[32] bp 130 °C); NMR (CCl_4) δ 1.15 (d, J = 6 Hz, 3), 2.4 (s, 1, OH by D_2O exchange), 3.4 (s) overlapped with 3.5 (m) for a 6-H total. Certain compounds were identified from mixtures of predictable product composition that were prepared by standard hydroboration–oxidation (HB–OX) techniques[33] as follows: 4-methoxy-1-butanol from HB–OX of 4-methoxy-1-butene, 1-methoxy-2-butanol from HB–OX of 1-methoxy-2-butene, 5-methoxy-1-pentanol from HB–OX of 5-methoxy-1-pentene, 4-methoxy-1-pentanol from HB–OX of 4-methoxy-1-pentene, 6-methoxy-1-hexanol from HB–OX of 6-methoxy-1-hexene, 5-methoxy-1-hexanol from HB–OX of 5-methoxy-1-hexene. Both 4-methoxy-1-pentene and 5-methoxy-1-hexene were prepared by the monomethoxymercuration–demercuration of 1,4-pentadiene and 1,5-hexadiene using $Hg(NO_3)_2$ as the mercury salt and a 4 h reaction time to hopefully allow for statistical product formation.[34] 4-Methoxy-1-pentene: bp 86 °C; n^{20}_D 1.3984 [lit.[35] (for the (R)-(–) enantiomer) bp 86–88 °C; n^{27}_D 1.3932]; 5-methoxy-1-hexene:[36] bp 110–112 °C. The other methoxy alcohols were prepared by OM–DM sequences.

5-Methoxy-2-pentanol: bp 77–78 °C (15 mm); n^{20}_D 1.4223 [lit.[35] bp 84–86 °C (30 mm); n^{22}_D 1.4210]; IR (neat) 2.86, 8.95 μm; NMR (CCl_4) δ 1.13 (d, J = 6 Hz, 3), 1.53 (m, 4), 3.32 (s) overlapped with 3.75 (m) for a 6-H total before D_2O exchange and 5 H after, 3.68 (m, 1, sharpens considerably after D_2O exchange).

4-Methoxy-2-butanol: bp 146–147 °C (lit.[37] bp 145 °C); IR (neat) 2.95 μm; NMR ($CDCl_3$) δ 1.05 (d, J = 6 Hz, 3), 1.57 (q, J = 6 Hz, 2), 3.27 (s, 3), 3.44 (t, J = 6 Hz, 2), 3.85 (m, 1).

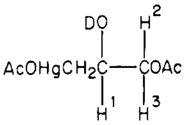
6-Methoxy-2-hexanol: bp 90–91 °C (12 mm); IR (neat) 2.95, 8.95 μm: NMR (CCl_4) δ 1.12 (d, J = 6 Hz, 3), 1..42 (m, 6), 2.9 (s, 1, OH by D_2O exchange), 3.26 (s) overlapped with 3.30 (m) for a 5-H total, 3.65 (m, 1, sharpens to a pentet, J = 6 Hz, after D_2O exchange).

Anal. Calcd for $C_7H_{16}O_2$: C, 63.60; H, 12.20. Found: C, 63.57; H, 12.41. With t_1 = 21 min and t_2 = 1 h, the product contained 21% residual 5-methoxycyclooctene and no detectable amount (<0.2%) of 8 or 11.

OM–DM of 5-Methoxycyclooctene. A sample of a mixture of ethers (8 and 11) was prepared by the dioxymercuration–demercuration of 1,5-cyclooctadiene, which is known to give these products. VPC analysis of the OM–DM reaction mixture from 5-methoxycyclooctene was first performed on a 6 ft × 0.25 in., 19.5% Carbowax 20M with 0.5% Armac 18D on 60/80 Chromosorb W AW/DMCS column to get the total absolute yield of all three ethers, i.e., residual 5-methoxycyclooctene plus 8 and 11, since they all overlap and appear as one peak under these VPC conditions. In order to get the distribution of the three ether products, we performed the analysis on a 12 ft × 0.125-in., 10% Glycerin on Varaport 30 100/120 column. Under these conditions, the 5-methoxycyclooctene elutes first and is base-line resolved from both 8 and 11 which partially overlap under these conditions.

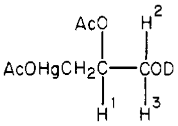
NMR Studies of the OM of Unsaturated Acetates. The following procedure was used. In a 1-dram vial were placed 4.0 mmol of mercuric acetate and 1 mL of D_2O, and then 4 mmol of the unsaturated acetate was added. The vial was capped with a Teflon-lined cap and then shaken vigorously, and some heat was evolved in the process. An aliquot was then placed into an NMR tube, the spectrum was recorded, and integrations were made with a digital integrator. For measurement of the chemical shifts, the sample was diluted with an equal volume of dimethyl sulfoxide, and chemical shifts were then determined with respect to Me_2SO. Me_2SO absorption was taken to be 153 Hz at 60 MHz from a separate determination of Me_4Si-saturated Me_2SO.

For allyl acetate, H^1, H_2, and H^3 of adduct 17 appeared as a complex multiplet between δ 3.6–4.2, whereas in 18, H^1 appeared as a pentet at δ 4.95 (J = 5 Hz), and H^2 and H^3 appeared as a doublet (J = 5 Hz) at δ 3.42. A double-resonance experiment, in which the δ 4.95 pentet was irradiated, caused the δ 3.42 doublet to collapse to a singlet. Although one would predict that the diacetoxy compound 19 which could arise from competitive acetate ion attack would be readily distinguishable by NMR from either 17 or 18, in order to test this possibility, we prepared 19 in situ by reacting allyl acetate with mercuric acetate in glacial acetic acid. The acetic acid solvent was pumped off under vacuum, D_2O added to the residue, and the spectrum recorded as above. Indeed, 19 was easily distinguishable from 17 or 18 in that H^1 of 19 appeared as a pentet (J = 6 Hz) at δ 5.17, and H^2 and H^3 appeared as a multiplet from δ 3.8 to 4.4. However, due to the proximity of the absorptions, the presence of small amounts of 19 (ca. 5%) could not be excluded in the OM reaction mixture of 17 and 18 from allyl acetate. No allyl acetate remained in the OM reaction mixture.



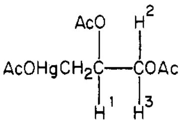
$AcOHgCH_2\underset{H^1}{\overset{DO}{C}}-\underset{H^3}{\overset{H^2}{C}}OAc$

17



$AcOHgCH_2\underset{H^1}{\overset{AcO}{C}}-\underset{H^3}{\overset{H^2}{C}}OD$

18



$AcOHgCH_2\underset{H^1}{\overset{AcO}{C}}-\underset{H^3}{\overset{H^2}{C}}OAc$

19

Due to the more complex nature of the products possible from the OM of crotyl acetate, the interchanged product 20 was prepared in situ by the acetoxymercuration of crotyl alcohol in like manner as above. The 20 thus obtained was apparently a mixture of diastereoisomers since two methyl doublets (J = 6 Hz) at δ 1.17 and 1.22 were observed. H^1 appeared at δ 5.08 (p, J = 6 Hz), H^2 at δ 2.90 (q, J = 6 Hz), and H^3 and H^4 at δ 3.72 (d, J = 6 Hz). The NMR spectrum from OM of crotyl acetate was consistent with 21 being the major product since a methyl doublet at δ 1.13 (J = 6 Hz) appeared and H^1 appeared at δ 3.95 (p, J = 6 Hz), H^2 at δ 2.88 (q, J = 6 Hz), and H^3 and H^4 at δ 4.35 (d, J = 6 Hz). Examination of the NMR spectrum from the OM of crotyl acetate on the high-field side of H^2 of 21 for H^3 and H^4 of 20 was possible and showed no significant amount (estimated less than 5%) of this species. Due to the complexity of the spectrum, however,

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[31] R. C. E. Elderfield, W. J. Gensler, F. Brody, J. C. Head, S. C. Dickerman, L. Wiederhold, III, C. B. Kremer, H. A. Hageman, F. J. Kreysa, J. M. Griffing, S. M. Kupchan, B. Newman, and J. T. Maynard, *J. Am. Chem. Soc.*, **68**, 1579 (1946).

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[33] H. C. Brown and M. K. Unni, *J. Am. Chem. Soc.*, **90**, 2902, 2906 (1968).

[34] H. C. Brown, P. J. Geoghegan, Jr., G. J. Lynch, and J. T. Kurek, *J. Org. Chem.*, **37**, 1941 (1972).

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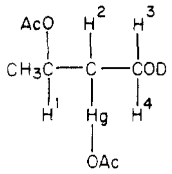
[37] W. Franke and D. Tietjen, German Patent 962787 (1957); *Chem. Abstr.*, **53**, 11235*f* (1959).



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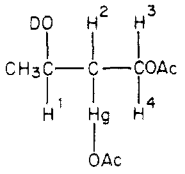

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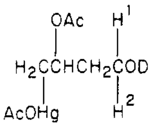

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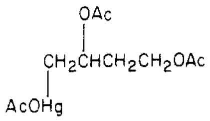

23

the presence of smaller quantities of **20** cannot be excluded. No crotyl acetate remained in the OM reaction mixture.

OM of 3-buten-1-yl acetate in a manner similar to that above showed the presence of 94% of the normal adduct. The remainder appeared to be a mixture of 2% of the acetoxy-interchanged mercurial **22** and 4% of the diacetoxy adduct **23**. However, the only evidence for **23** and the only basis of assigning a percentage to it was the integration of the CHOAc pentet at ca. δ 5.05, which integrated too high relative to the δ 3.46 triplet of H^1 and H_2 of **22** to be accounted for only on the basis of this material. Consequently, the presence of **23** was assumed.

Registry No. 1 (X = OH), 107-18-6; 1 (X = OCH_3), 627-40-7; 1 (X = OAc), 591-87-7; 2 (X = OH), 6117-91-5; *cis*-2 (X = OCH_3), 10034-16-9; *trans*-2 (X = OCH_3), 10034-14-7; 2 (X = OAc), 628-08-0; 3 (X = OH), 627-27-0; 3 (X = OCH_3), 4696-30-4; 3 (X = OAc), 1576-84-7; 4 (X = OH), 821-09-0; 4 (X = OCH_3), 1191-31-7; 4 (X = OAc), 1576-85-8; 5 (X = OH), 821-41-0; 5 (X = OCH_3), 5084-33-3; 5 (X = OAc), 5048-26-0; 6, 32160-45-5; 17, 75919-11-8; 18, 75919-12-9; 19, 75919-13-0; 20 (isomer 1), 75919-14-1; 20 (isomer 2), 75919-15-2; 21, 75919-16-3; 22, 75919-17-4; 23, 75919-18-5; 1-methoxy-2-propanol, 107-98-2; 1-methoxy-3-propanol, 1589-49-7; 4-methoxy-1-butanol, 111-32-0; 1-methoxy-2-butanol, 53778-73-7; 5-methoxy-1-pentanol, 4799-62-6; 6-methoxy-1-hexanol, 57021-65-5; 1,2-propanediol, 57-55-6; 1,3-propanediol, 504-63-2; 1,3-butanediol, 107-88-0; 1,4-butanediol, 110-63-4; tetrahydrofuran, 109-99-9; 1,2-butanediol, 584-03-2; 2-methyltetrahydrofuran, 96-47-9; 1,4-pentanediol, 626-95-9; 1,5-pentanediol, 111-29-5; 1,5-hexanediol, 928-40-5; 1,6-hexanediol, 629-11-8; 2,3-butanediol, 513-85-9; 1,5-cyclooctadiene, 111-78-4; 5-methoxy-2-pentanol, 18423-18-2; 4-methoxy-2-butanol, 41223-27-2; 6-methoxy-2-hexanol, 75919-19-6.

Formation of Peralkylcyclohexadienyllithium Compounds

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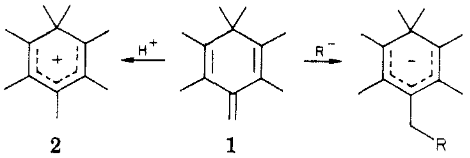
Received July 18, 1980

1,1,2,3,5,6-Hexamethyl-4-methylene-2,5-cyclohexadiene (**1**) reacts with alkyllithium compounds, RLi (R = *n*-Bu, *sec*-Bu, and *t*-Bu), at 20 °C in hydrocarbon solution or in the presence of ethers or tertiary amines, which act as ligands, to give stable, soluble 1,1,2,3,5,6-hexamethyl-4-alkylcyclohexadienyllithium compounds, **3a–c**. On heating, the latter aromatize to pentamethylalkylbenzenes, **4a–c**, with extrusion of methyllithium, while on hydrolysis of **3a–c** isomeric substituted cyclohexadienes are obtained. The effects have been investigated of varying RLi structure, ligand, and temperature on the rates of addition and aromatization reactions. Ligand metalation by RLi is a significant side reaction. Addition is faster with ligands known to reduce the association of alkyllithium compounds. Aromatization is faster in the presence of THF which favors formation of loose ion pairs and is slower with heavy substitution on the ring. It is proposed that large substituents (neopentyl) destabilize the transition states for aromatization due to steric interactions.

Introduction

In the study of ion pairing[1] in and among salts which contain carbanions, it would be desirable to find systems which form stable solutions in a variety of solvents and over a wide temperature range. In practice this is rarely achieved and thus many carbanion salts and their complexes are not amenable to solution spectroscopic investigation, specifically with NMR methods. This restriction has now been lifted with a series of substituted cyclohexadienylic lithium compounds.

The compound 1,1,2,3,5,6-hexamethyl-4-methylene-2,5-cyclohexadiene, **1**, is best known as the precursor of the heptamethylbenzenium ion,[2] **2**. We have now investigated the possible corresponding reaction with carbanionic substances. Ample precedent exists for the addition of organolithium compounds to polyenes.[3] It will be shown how alkyllithium compounds add to the methylene carbon of **1** to give stable soluble cyclohexadienylic lithium compounds both in the presence of ligands and unsolvated. This development makes possible comparative studies of ion-pairing effects in closely related anions and cations.[4] This paper mainly concerns the qualitative aspects of the reaction of triene **1** with different alkyllithium compounds—the effect of temperature and lithium ligands and an interesting aromatization reaction which involves the extrusion of methyllithium.



2 **1** **3**

The list of abbreviations for lithium ligands is found at the beginning of the Experimental Section.

Results and Discussion

General Observations. Triene **1** was found to react smoothly at room temperature with alkyllithium com-

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