methanol–ether: λ_{max}^{EtOH} 417 nm (ϵ 3.42 × 10^4).

Anal. Calcd for $C_{23}H_{28}N_2SO_3$: C, 66.99; H, 6.80; N, 6.80. Found: C, 66.26; H, 6.87; N, 6.54.

1-(3-Sulfonatopropyl)-4-[β-(1-*n*-butyl-5-indolyl)vinyl]pyridinium betaine (30a) was prepared from **29** and sultone **21a** in 70% yield: mp 248–250 °C; λ_{max}^{EtOH} 427 nm (ϵ 3.12 × 10^4).

1-(3-Sulfonatopropyl)-4-[β-[2-(di-*n*-butylamino)-6-naphthyl]vinyl]pyridinium Betaine (27a). To 1 g (0.008 mol) of 1,3-propanesultone in 5 mL of CH_2Cl_2 was added 1 g (0.028 mol) of **26** and the mixture was stirred for 24 h at 20 °C. Upon cooling for 24 h, **26** precipitated as a red solid and was crystallized from methanol–ether or purified by chromatography on silica gel: 0.75 g (56%); mp 122–124 °C; λ_{max}^{EtOH} 495 nm (ϵ 3.05 × 10^4).

Anal. Calcd for $C_{28}H_{36}N_2SO_3$: C, 69.97; H, 7.55. Found: C, 69.74; H, 7.58.

1-(3-Sulfonatopropyl)-4-[β-[p'-(di-*n*-butylamino)-*p*-stilbenyl]vinyl]pyridinium betaine (34) was prepared in 46% yield by refluxing 1,3-propanesulftone (**21a**) and pyridine **33** in CH_2Cl_2 for 16 h; **34** crystallized as a black solid: mp >300 °C; λ_{max}^{EtOH} 482 nm (ϵ 3.83 × 10^4).

Anal. Calcd for $C_{32}H_{40}N_2SO_3$: C, 72.18; H, 7.52; N, 5.26. Found: C, 70.96; H, 7.64; N, 5.11.

1-(2-Carboxyethyl)-4-[*p*-(di-*n*-butylamino)styryl]pyridinium betaine (22a) was obtained by refluxing 1 g (0.0032 mol) of **20b** and 0.7 g (0.004 mol) of sodium 3-bromopropanoate in 30 mL of absolute ethanol for 16 h. Chromatography of the resulting oil on silica gel and elution with ethyl acetate–ethanol (6:4) gave 0.6 g of **22a** (48%) as a red solid: mp 156–157 °C; MS, *m/e* (relative intensity) 308 (51.1, M – $C_3H_4O_2$), 265 (100, 308 – C_3H_7); λ_{max}^{EtOH} 486 nm (ϵ 3.92 × 10^4). The identical product (**22a**) was obtained by reaction of **20b** with β-propiolactone.

1-(Carbethoxymethyl)-4-[*p*-(di-*n*-butylamino)styryl]pyridinium bromide (22b) was prepared in 51% yield by refluxing **20b** with 1.2 equiv of ethyl bromoacetate in dry benzene and crystallization from ethanol–hexane: mp 160–162 °C; λ_{max}^{EtOH} 507 nm (ϵ 5.31 × 10^4).

Anal. Calcd for $C_{25}H_{25}N_2O_2Br$: C, 63.15; H, 7.42; N, 5.89. Found: C, 61.96; H, 7.27; N, 5.85.

1-[γ-(Isothiocyanato)propyl]-4-[*p*-(dibutylamino)-styryl]pyridinium Bromide (23). A solution of 1 g (0.0032 mol) of **20b** and 2 mL of 3-bromopropylisothiocyanate in 50 mL of acetone (analytical grade) was allowed to stand for 16 h. The red solid was crystallized from acetone–hexane to give 0.95 g (60%) of **23**: mp 148–150 °C; IR 2100 cm^{-1} (N=C=S); λ_{max}^{EtOH} 500 nm (ϵ 5.28 × 10^4).

Anal. Calcd for $C_{25}H_{34}N_3BrS$: C, 61.47; H, 6.97; N, 8.61. Found: C, 59.94; H, 7.49; N, 8.46.

General Procedure for Aldol Coupling. Synthesis of 1-(4-Sulfonatobutyl)-4-[*p*-(di-*n*-hexylamino)styryl]pyridinium Betaine (1b). A solution of 3 g (0.01 mol) of 4-(di-*n*-hexylamino)benzaldehyde (**3a**), 3 g (0.013 mol) of 1-(4-sulfonatobutyl)-4-picolinium betaine (**2b**) and 1 mL of pyrrolidine in 30 mL of absolute ethanol was refluxed for 16 h. After cooling at 5 °C for 1 h, the orange solid was filtered and then purified by chromatography on silica gel (elution with ethyl acetate–ethanol (1:1) to furnish 3 g (60%) of **1b**: mp 310–312 °C; λ_{max}^{EtOH} 495 nm (ϵ 3.41 × 10^4).

Anal. Calcd for $C_{29}H_{44}N_2SO_3$: C, 69.56; H, 8.86; N, 5.59. Found: C, 69.41; H, 8.88; N, 5.52.

The other compounds in Tables I and II were prepared by this procedure and gave satisfactory analyses. The nmr spectrum of *1d* is described in Figure 1 and indicates an *E* (trans) stereochemistry about the double bond.

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Registry No. **1a**, 77673-49-5; **1b**, 90133-77-0; **1c**, 86691-58-9; (*E*)-**1d**, 90133-78-1; **1e**, 83683-58-3; **2a**, 15626-30-9; **2b**, 90133-79-2; **2c-I**, 2301-80-6; **3a**, 90133-80-5; **4a**, 90133-81-6; **4b**, 90133-82-7; **5b**, 83668-96-6; **5c**, 90133-83-8; **5d**, 90133-84-9; **6**, 90133-85-0; **7a**, 90133-86-1; **7b**, 90171-25-8; **7c**, 90133-87-2; **8**, 90133-88-3; **9**, 90133-89-4; **10**, 90133-90-7; **11**, 90133-91-8; **12**, 90133-92-9; **16** (R = Bu), 53358-54-6; **16c**, 90133-93-0; **18**, 100-43-6; (*E*)-**20b**, 90133-94-1; **21a**, 1120-71-4; **22a**, 90133-95-2; **22b**, 90133-96-3; **23**, 90133-97-4; **25a**, 7499-66-3; **25b**, 90133-98-5; **26**, 90133-99-6; **27a**, 90134-00-2; **27b**, 90134-01-3; **28**, 90134-02-4; **29**, 90134-03-5; **30a**, 90134-04-6; **30b**, 90134-05-7; **32a**, 90134-06-8; **32b**, 90134-07-9; **33**, 90134-08-0; *p*-iodo-*N*,*N*-di-*n*-hexylaniline, 90134-09-1; sodium 3-bromopropanoate, 43165-24-8; 4-(dibutylamino)benzaldehyde, 90134-10-4; 4-(dibutylamino)cinnamaldehyde, 90134-11-5; 4-(dihexylamino)cinnamaldehyde, 90134-12-6; 9-ethyl-3-formylcarbazole, 7570-45-8; 9-formyl-2,3,6,7-tetrahydro-[1*H*,5*H*]benzo[*ij*]quinolizine, 33985-71-6; 1-(3-sulfopropyl)-4-ethylpyridinium, 90134-13-7; 1-(3-sulfopropyl)-4-methylquinolinium, 56405-66-4; 1-(3-sulfopropyl)-6-methylquinolinium, 90134-14-8; 1-(3-sulfopropyl)-2-methylpyridinium, 56405-61-9; 4-bromostyrene, 2039-82-9; 3-bromopropyl isothiocyanate, 2799-73-7; 1-methylpyrrole-2-carboxaldehyde, 1192-58-1.

Solvomercuration–Demercuration. 11. Alkoxymercuration–Demercuration of Representative Alkenes in Alcohol Solvents with the Mercuric Salts Acetate, Trifluoroacetate, Nitrate, and Methanesulfonate

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The alkoxymercuration–demercuration of seven representative olefins with the mercuric salts acetate, trifluoroacetate, nitrate, and methanesulfonate, in methyl, ethyl, isopropyl, and *tert*-butyl alcohols was examined. Mercuric acetate was effective only in methanol and ethanol. On the other hand, mercuric trifluoroacetate was effective in all four solvents, giving in most cases high yields of the corresponding ethers. Both mercuric nitrate and mercuric methanesulfonate were effective in methanol, ethanol, and 2-propanol. However, in several cases poor selectivity for the ether was observed, as evidenced by the formation of significant amounts of side products. Both electronic and steric effects are important factors in the reaction. Moreover, the structure of the olefin has a pronounced effect, both on the types of oxymercurials formed and on their stability to the reaction conditions.

The oxy(solvo)mercuration of olefins has been extensively studied since the turn of the century.[1-3] The major thrust of the work has been mechanistically oriented. This reaction became a major synthetic tool when it was dis-

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Scheme I

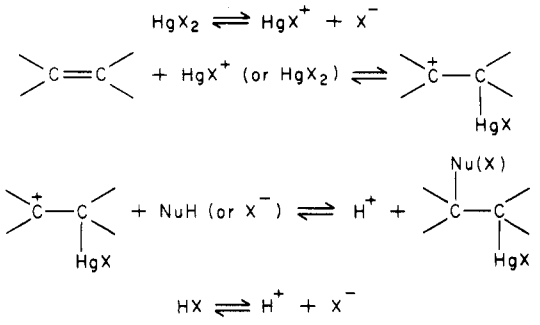

Table I. Alkoxymercuration–Demercuration of 1-Hexene

ROH	HgX_2	time,[b] min	% products[a] 2-OR	2-OH	1-OR
CH_3OH	$Hg(OAc)_2$	5–60	84	0	0
	$Hg(TFA)_2$	5–60	90	0	0
	$Hg(NO_3)_2$	5–60	86	0	0
	$Hg(OMs)_2$	5–60	83	0	0
CH_3CH_2OH	$Hg(OAc)_2$	5–60	98	0	0
	$Hg(TFA)_2$	5–60	97	0	0
	$Hg(NO_3)_2$	5–60	100	0	0
	$Hg(OMs)_2$[c]	5–60	96	0	0
$(CH_3)_2CHOH$	$Hg(OAc)_2$	5–60	67	2	0
	$Hg(TFA)_2$	5–60	94	1	0
	$Hg(NO_3)_2$	5–60	84	4	0
	$Hg(OMs)_2$[c]	5	77	0	0
		60	91	0	0
$(CH_3)_3COH$	$Hg(OAc)_2$	60	5	4	3
		1440	39	25	15
	$Hg(TFA)_2$	5–60	82	14	1
	$Hg(NO_3)_2$	5	34	23	1
		180	24	25	1
	$Hg(OMs)_2$	5	21	25	1
		60	48	26	1

[a] Remainder of material balance was 1-hexene with the exception of reactions in *tert*-butyl alcohol where this yield was low. [b] Product yields were identical within experimental error for the time span indicated. [c] See Experimental Section.

covered that oxymercurials could be demercurated in situ with aqueous alkaline sodium borohydride.[4,5] Since then, the solvomercuration–demercuration (SM–DM) of olefins has been employed to synthesize ethers,[6] acetamides,[7] formamides,[8] amines,[9] peroxides,[10] and azides,[11] along with numerous carbocyclic[12,13] and heterocyclic molecules.[14-17]

Table II. Alkoxymercuration–Demercuration of Styrene

ROH	HgX_2	time,[a] min	% products 2-OR	2-OH	styrene[b]
CH_3OH	$Hg(OAc)_2$	5–60	93	0	2
	$Hg(TFA)_2$	5–60	96	0	1
	$Hg(NO_3)_2$	5–60	97	0	2
	$Hg(OMs)_2$	5–60	94	0	2
CH_3CH_2OH	$Hg(OAc)_2$	5	79	0	13
		60	90	0	13
	$Hg(TFA)_2$	5–60	100	0	6
	$Hg(NO_3)_2$	5–60	83	0	12
	$Hg(OMs)_2$[c]	5–60	70	0	17
$(CH_3)_2CHOH$	$Hg(OAc)_2$	60	47	4	49
		120	65	10	16
	$Hg(TFA)_2$	5	85	3	6
		60	92	0	2
	$Hg(NO_3)_2$	5–60	86	3	10
	$Hg(OMs)_2$[c]	5	46	5	34
		60	82	trace	16
$(CH_3)_3COH$	$Hg(OAc)_2$	60	2	trace	91
		1200	32	9	47
	$Hg(TFA)_2$	5–60	87	2	7
	$Hg(NO_3)_2$	5	27	7	44
		60	12	6	38
		720	trace	3	58
	$Hg(OMs)_2$	5	7	8	66
		60	20	37	17
		1440	trace	trace	65

[a] Product yields were identical within experimental error for the time span indicated. [b] GLC analyses of styrene were sometimes erratic. [c] See Experimental Section.

Table III. Alkoxymercuration–Demercuration of *tert*-Butylethylene

ROH	HgX_2	time,[a] min	% products 2-OR	1-OR	2-OH
CH_3OH	$Hg(OAc)_2$	5–60	83	2	0
	$Hg(TFA)_2$	5–60	86	4	0
	$Hg(NO_3)_2$	5–60	89	5	0
	$Hg(OMs)_2$	5–60	91	1	0
CH_3CH_2OH	$Hg(OAc)_2$	120–240	67	3	3
	$Hg(TFA)_2$	5–60	83	3	1
	$Hg(NO_3)_2$	5–60	85	6	2
	$Hg(OMs)_2$	5–60	82	4	0
$(CH_3)_2CHOH$	$Hg(OAc)_2$	120	trace	0	0
	$Hg(TFA)_2$	5	53	10	27
		60	67	13	10
	$Hg(NO_3)_2$	5	62	13	13
		60	78	7	11
	$Hg(OMs)_2$[b]	5	31	7	2
		60	74	7	0
$(CH_3)_3COH$	$Hg(OAc)_2$	60	trace	trace	trace
		1440	trace	trace	trace
	$Hg(TFA)_2$	5	21	17	51
		60	24	24	34
		1440	34	27	10
	$Hg(NO_3)_2$	5	5	4	6
		60	9	8	53
		1440	9	8	54
	$Hg(OMs)_2$	5	2	1	15
		60	11	8	34
		1440	6	4	23

[a] Product yields were identical within experimental error over the time span indicated. [b] See Experimental Section.

Moreover, the SM–DM technique has been employed in the study of various functional groups, kinetics, and

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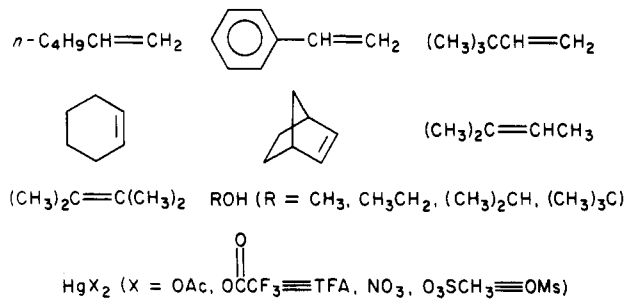
Chart I



stereochemistry. Indeed, Seyferth's annual reviews[18] provide ample evidence that this is a highly active area of research.

It is generally believed that the solvomercuration of olefins in protic solvents proceeds through a series of reversible reactions[19] depicted in Scheme I. The overall success of the reaction can depend on several variables, such as the mercuric salt and the reactivity of the electrophile, along with the strength of the acid generated and the reactivity (nucleophilicity) of the gegenion, X^-. Also, the nature of the solvent with regard to its nucleophilicity is important. Of equal significance is the structure of the olefin and its effect on the various species involved in the solvomercuration reaction.

To date, there have been no studies directed at an understanding of all of these variables and their interdependent effects on the alkoxymercuration reaction. Accordingly, we undertook such a study.

Results and Discussion

The alkoxymercuration–demercuration (ROM–DM) of seven representative olefins with four mercuric salts in four alcohol solvents was examined (Chart I).

Monosubstituted Olefins. The results for the ROM–DM of 1-hexene, styrene, and *tert*-butylethylene are summarized in Tables I–III. The ROM of these olefins in methanol and ethanol is rapid and usually complete within 5 min for all four mercuric salts. The only products in most cases following DM are the Markovnikov ethers.

In 2-propanol, differences in results for various mercuric salts are evident. Mercuric acetate reacts at a noticeably slower rate in this solvent than in methanol and ethanol. The mercuric salts of the strong acids, however, react quite rapidly.

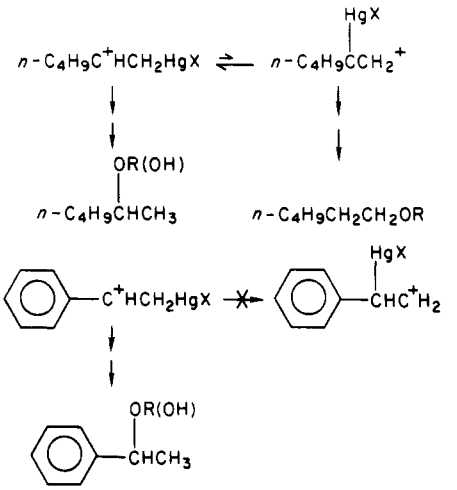
The major products in all cases are the Markovnikov ethers. However, a loss of selectivity is also observed. 1-Hexene gives small amounts of 2-hexanol. Similar behavior is found for styrene. The sterically hindered *tert*-butylethylene gives significant yields of both the secondary alcohol and the primary ether.

The formation of Markovnikov alcohols apparently arises from concurrent capture of a hydrolyzable anion by the β-mercurated cation. Hydrolysis to the alcohol then occurs during the demercuration step (eq 1).

$$RC^+HCH_2HgX \xrightarrow[(X = OAc, TFA, NO_3, OMs)]{X^-} RCXHCH_2HgX \xrightarrow{DM} RCH(OH)CH_3 \quad (1)$$

The ROM of monosubstituted olefins in *tert*-butyl alcohol is strongly dependent both on the mercuric salt and the structure of the olefin. Mercuric trifluoroacetate exhibits very high selectivity for the Markovnikov ethers with 1-hexene and styrene. Moreover, the reactions are quite rapid, being complete within 5 min. Mercuric acetate reacts much more slowly, with poor selectivity for the secondary ethers. The other salts react rapidly, but again, with poor selectivity. Significantly poorer conversions are realized with both mercuric nitrate and methanesulfonate, indicating less favorable equilibria.

Electronic factors are clearly important in the ROM of olefins in alcohols. 1-Hexene in *tert*-butyl alcohol gives, in addition to the secondary ether and secondary alcohol, small amounts of the primary ether. On the other hand, styrene undergoes reaction to give only Markovnikov products. This can be rationalized in terms of the difference in the electronic effects of the *n*-alkyl group and the phenyl group in stabilizing the cationic intermediates (eq 2 and 3).



An examination of the results for the ROM of *tert*-butylethylene clearly reveals the significance of steric factors. Even in methanol, there is observed the formation of small amounts of primary ether. Moreover, a comparison of the ether (secondary and primary) alcohol product ratios in 2-propanol and *tert*-butyl alcohol reveals that the alkoxymercurials are equilibrating with time. This equilibration is usually in the direction of the β-mercurated ether (eq 4).

$$(CH_3)_3CCXHCH_2HgX \rightleftharpoons (CH_3)_3CC(OR)HCH_2HgX + (CH_3)_3CC(HgX)HCH_2OR \quad (4)$$

In addition, a comparison of the initial ether (secondary and primary) alcohol ratios reveals the following order of gegenion nucleophilicity in *tert*-butyl alcohol:

$$OAc > TFA > NO_3 > OMs$$

1,2-Disubstituted Olefins. The results for the ROM–DM of cyclohexene and norbornene are summarized in Tables IV and V. The ROM of cyclohexene in methanol and ethanol is very fast with all four mercuric salts. The

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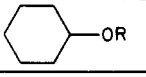
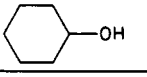
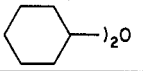
Table IV. Alkoxymercuration-Demercuration of Cyclohexene

ROH	HgX_2	time,[a] min	% products			
						
CH_3OH	$Hg(OAc)_2$	5–60	98	0	0	0
	$Hg(TFA)_2$	5–60	92	0	0	0
	$Hg(NO_3)_2$	5–60	100	0	0	0
	$Hg(OMs)_2$	5–60	96	0	0	0
CH_3CH_2OH	$Hg(OAc)_2$	5–60	83	0	0	17
	$Hg(TFA)_2$	5–60	100	0	0	0
	$Hg(NO_3)_2$	5–60	100	0	0	0
	$Hg(OMs)_2$[b]	5	81	0	0	23
		15–60	95	0	0	6
$(CH_3)_3CHOH$	$Hg(OAc)_2$	60	30	10	0	51
		120	43	11	0	30
		300	60	17	0	13
	$Hg(TFA)_2$	5–60	95	2	0	2
	$Hg(NO_3)_2$	5–60	96	4	0	3
	$Hg(OMs)_2$[b]	5	64	4	0	23
		30[c]	86	trace	0	20
$(CH_3)_3COH$	$Hg(OAc)_2$	60	0	0	0	80
	$Hg(TFA)_2$	5–60	89	6	1	4
	$Hg(NO_3)_2$	5	14	11	3	60
		60	4	7	76	2
	$Hg(OMs)_2$	5	7	63	3	13
		60	12	43	4	19

[a] Product yields were identical within experimental error during the time span indicated. [b] See Experimental Section. [c] Oxymercurial percipitated out of solution at this point to the extent that efficient stirring was no longer possible.

Table V. Alkoxymercuration-Demercuration of Norbornene

ROH	HgX_2	time,[a] min	% products			
			exo OR	exo OH	exo X	norbornene
CH_3OH	$Hg(OAc)_2$	5–60	78	7	0	0
	$Hg(TFA)_2$	5–60	91	3	0	0
	$Hg(NO_3)_2$	5–60	91	0	0	0
	$Hg(OMs)_2$	5–60	95	0	0	0
CH_3CH_2OH	$Hg(OAc)_2$	5–60	32	42	0	4
	$Hg(TFA)_2$	5–60	73	11	0	3
	$Hg(NO_3)_2$	5–60	92	4	0	1
	$Hg(OMs)_2$[b]	5–60	81	0	0	2
$(CH_3)_2CHOH$	$Hg(OAc)_2$	5–60	6	56	16	14
	$Hg(TFA)_2$	5	29	65	0	1
		60	40	57	0	3
		1440	47	50	0	0
	$Hg(NO_3)_2$	5	47	16	0	32
		60	81	17	0	trace
		1440	97	3	0	0
	$Hg(OMs)_2$[b]	5	72	4	0	0
		60	94	3	0	0
$(CH_3)_3COH$	$Hg(OAc)_2$	5	trace	11	29	62
		60	1	22	65	17
		1440	1	11	58	20
	$Hg(TFA)_2$	5	8	70	0	4
		60	21	66	0	2
		1440	84	10	0	1
	$Hg(NO_3)_2$	5	15	28	0	55
		60	46	36	0	18
		1440	63	25	0	3
	$Hg(OMs)_2$	5	20	12	0	65
		60	95	3	0	5

[a] Product yields were identical within experimental error during the time span indicated. [b] See Experimental Section.

only products observed are the corresponding ethers. In 2-propanol, the major product is the isopropyl ether. However, small amounts of cyclohexanol are also observed.

The results for the ROM of cyclohexene in *tert*-butyl alcohol are different for each mercuric salt. The acetate reaction is very slow and no reaction products are observable within 1 h. On the other hand, the salts of the strong acids react rapidly to give varying amounts of *tert*-butyl cyclohexyl ether, cyclohexanol, and dicyclohexyl ether. The major product from mercuric trifluoroacetate is the *tert*-butyl ether. Cyclohexanol is the major product from the methanesulfonate and dicyclohexyl ether is the major product from the nitrate.

The ROM–DM of norbornene in methanol and ethanol gives as the major products the exo ethers along with smaller amounts of *exo*-norbornanol. This is not the case in 2-propanol. Mercuric acetate gives as the major product the exo alcohol along with smaller amounts of the exo

Table VI. Alkoxymercuration–Demercuration of 2-Methyl-2-butene

ROH	HgX_2	time,[a] min	% products 2-OR	% products 2-OH
CH_3OH	$Hg(OAc)_2$	5–60	93	0
	$Hg(TFA)_2$	5	72	0
		60	38	0
	$Hg(NO_3)_2$	5	44	0
		60	7	0
	$Hg(OMs)_2$	1	34	0
		5	9	0
		60	0	0
CH_3CH_2OH	$Hg(OAc)_2$	5–60	86	0
	$Hg(TFA)_2$	5	56	2
		15	40	1
		30	36	1
	$Hg(NO_3)_2$	5	30	6
		15	14	5
		30	4	trace
	$Hg(OMs)_2$[b]	5	30	trace
		30	3	0
$(CH_3)_2CHOH$	$Hg(OAc)_2$	5	trace	trace
		1440	32	5
	$Hg(TFA)_2$	5	27	6
		30	6	3
	$Hg(NO_3)_2$	5	4	14
		30	0	trace
	$Hg(OMs)_2$[b]	5	2	50
		30	0	39
$(CH_3)_3COH$	$Hg(OAc)_2$	5–180	0	0
	$Hg(TFA)_2$	5–180	0	0
	$Hg(NO_3)_2$	5–180	0	0
	$Hg(OMs)_2$	5	0	71
		60	0	83
		180	0	75

[a] Product yields were identical within experimental error during the time span indicated. [b] See Experimental Section.

acetate. Evidently the hydrolysis of the acetate in the demercuration step is more difficult in this system than in others, so some of the acetate persists. The oxymercurials from the other three mercuric salts clearly equilibrate with time, as is indicated by the ether–alcohol product ratios. It is interesting that with mercuric trifluoroacetate this equilibrium is ca. 50:50, while with the nitrate and methanesulfonate, it is ca. 94–97.3.

The ROM–DM of norbornene in *tert*-butyl alcohol exhibits essentially the same characteristics as those in 2-propanol.

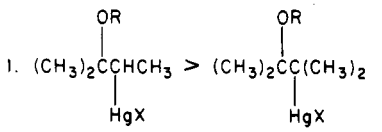
A comparison of the initial ether–alcohol ratios in ethanol, 2-propanol, and *tert*-butyl alcohol indicates once again the order of gegenion nucleophilicity:

$$OAc > TFA > NO_3 > OMs$$

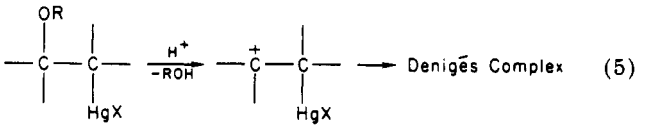
It is of significance that even in *tert*-butyl alcohol the only products observed resulted from exo attack on the β-mercurated intermediate. No endo products or tricyclyl products could be detected.

Tri- and Tetrasubstituted Olefins. The results for the ROM–DM of 2-methyl-2-butene and tetramethylethylene are summarized in Tables VI–XI. Mercuric acetate exhibited the same behavior with these two olefins as it did with previous ones. However, the results using the mercuric salts of the strong acids were remarkably different.

An examination of the results for the ROM–DM of these olefins clearly indicates that the alkoxymercurials initially formed are unstable with respect to time. Moreover, these results indicate the following orders of stabilities for the alkoxymercurials:

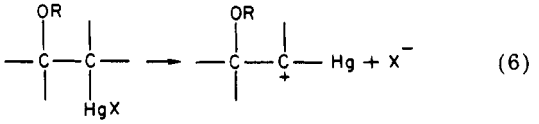


It is also significant that in all of these reactions a yellow-colored species was observed, consistent with the Denigés complex[20] (eq 5).



(5)

However, these oxymercurials can also decompose by another pathway, solvolysis of the mercury group[21] (eq 6).



(6)

GLC analysis of these reaction mixtures revealed several other products, but in extremely small trace amounts. Consequently, if the solvolytic pathway is operational, it is clearly of little significance.

In our earlier studies[5b] on the oxymercuration–demercuration of olefins in aqueous tetrahydrofuran, we observed similar behavior for tri- and tetrasubstituted olefins. Fortunately, the stability of the oxymercurials could be markedly improved by merely conducting the reaction at 0 °C, as opposed to the usual room temperature (22–25 °C). Consequently, we reexamined these solvomercurations at 0 °C in methanol, ethanol, and 2-propanol. Indeed, major improvement in the stability of the intermediates was observed. Mercuric trifluoroacetate, as expected, produced more stable mercurials than did mercuric nitrate and methanesulfonate (Tables VIII and IX).

Summary and Conclusions

This study has elucidated several significant features of the solvomercuration of olefins in protic solvents.

Overall, the four mercuric salts exhibit markedly different behavior. Mercuric acetate is effective only in methanol and ethanol. In 2-propanol and *tert*-butyl alcohol, much slower reaction rates are observed in addition to unfavorable equilibria.

On the other hand, mercuric trifluoroacetate is extraordinarily effective in all four alcohol solvents, giving high yields of ethers in most cases. By running the solvomercuration at 0 °C, even ethers of tri- and tetrasubstituted olefins can be obtained, in most cases, in reasonable to excellent yields.

The mercuric salts nitrate and methanesulfonate however, are effective in methanol, ethanol, and 2-propanol only. In *tert*-butyl alcohol, major amounts of side products are observed, which depend solely (or at least in large part) on the olefinic structure. Also, these salts exhibit a somewhat diminished reaction rate in 2-propanol and *tert*-butyl alcohol, compared to the other two solvents.

Both electronic and steric factors are very important, especially for solvomercuration conducted in nucleophilic

(20) Ichikawa, K.; Fujita, K.; Itoh, O. *Bull. Inst. Chem. Res. Kyoto Univ.* **1964**, *42*, 221.
(21) Jensen, F. R.; Oulette, R. J. *J. Am. Chem. Soc.* **1963**, *85*, 363, 367.

Table VII. Alkoxymercuration–Demercuration of Tetramethylethylene (TME)

ROH	HgX_2	time, min	R'OR	R'OH	TME
CH_3OH	$Hg(OAc)_2$	5	32	0	57
		60	77	0	17
		120	81	0	15
	$Hg(TFA)_2$[a]	5	48	0	30
		30	26	0	36
		60	10	0	40
	$Hg(NO_3)_2$[a]	2	9	0	41
		5	2	0	40
		30	0	0	37
	$Hg(OMs)_2$[a]5	5	1	0	57
		30	1	0	46
		60	1	0	48
CH_3CH_2OH	$Hg(OAc)_2$	5	trace	0	99
		60	6	0	72
		1170	39	0	40
	$Hg(TFA)_2$[a]	5	32	3	20
		30	14	3	28
	$Hg(NO_3)_2$[a]	5	11	3	48
		15	11	3	42
		30	11	3	50
	$Hg(OMs)_2$[a,b]	5	14	2	66
		30	3	2	67
$(CH_3)_2CHOH$	$Hg(OAc)_2$	60–1440	0	0	100
	$Hg(TFA)_2$[a]	5	19	18	49
		30	6	18	52
	$Hg(NO_3)_2$[a]	5	1	14	74
		30	trace	13	78
	$Hg(OMs)_2$[a,b]	5	1	2	87
		30	trace	4	92
$(CH_3)_3COH$	$Hg(OAc)_2$	5	0	0	100
		60	0	0	98
	$Hg(TFA)_2$[a]	5	0	14	81
		60	0	8	73
	$Hg(NO_3)_2$[a]	5	0	6	86
		60	0	13	77
	$Hg(OMs)_2$[a]	5	0	7	83
		60	0	7	87

[a] Yellow Denigès complex observed. [b] See Experimental Section.

Table VIII. Alkoxymercuration–Demercuration of 2-Methyl-2-butene in Ethanol at 0 °C

		% products	
HgX_2	time, min	2-OEt	2-OH
$Hg(TFA)_2$	5–30	88	trace
$Hg(NO_3)_2$	5–30	61	20
$Hg(OMs)_2$	5	51	2
	30	40	2

Table IX. Alkoxymercuration–Demercuration of Tetramethylethylene in Ethanol at 0 °C (TME)

HgX_2	time, min	R'OR	R'OH	TME
$Hg(TFA)_2$	5–30	59	6	16
$Hg(NO_3)_2$	5	18	26	31
	30	21	9	53
$Hg(OMs)_2$	5	31	4	66
	30	19	6	60

Table X. Alkoxymercuration–Demercuration of 2-Methyl-2-butene with Mercuric Trifluoroacetate at 0 °C

ROH	time, min	2-OR	2-OH
CH_3OH	5–30	89	0
$(CH_3)_2CHOH$	5	50	28
	30	32	28

solvents of significant steric requirements, i.e., *tert*-butyl alcohol.

Table XI. Alkoxymercuration–Demercuration of Tetramethylethylene with Mercuric Trifluoroacetate at 0 °C (TME)

ROH	time, min	R'OR	R'OH	TME
CH_3OH	5	82	3	
	30	74	6	
$(CH_3)_2CHOH$	5	26	27	62
	30	18	19	54

Finally, the possible effects of various olefinic structures have been shown to be significant, and in some cases, impossible to predict, being interdependent with the effects of the solvent, nucleophile, and the mercuric salt.

Experimental Section

Mercuric acetate was commercially available (Baker, Fisher) and was used as received. Mercuric trifluoroacetate was synthesized as previously described.[6] Mercuric methanesulfonate was synthesized as follows: to 25 mL of distilled water was added freshly distilled methanesulfonic acid (8.14 g, 84.7 mmol). The solution was heated and to it was added red mercuric oxide (8.33 g, 38.5 mmol). Heating was maintained at 75 °C until all of the mercuric oxide had dissolved. The water was distilled off under vacuum to yield a crude white solid, which was then washed with either diethyl ether, chloroform, or *n*-hexane (distilled from $LiAlH_4$). The washed solid was then heated from 100–130 °C (0.02 mmHg) until no further water could be collected. The white solid had a mp of 272–274 °C and analyzed correctly for mercury. This procedure has been scaled up to 0.5 mol with no difficulty.

The olefins were all commercially available and were used as received after checking their purity by GLC analysis. The olefins were stored under prepurified nitrogen (Airco) and transferred to the reaction flasks via syringe. When purification was required, the olefins were stirred over $LiAlH_4$ for at least 3 h and then distilled under nitrogen.

Methanol was spectral grade (Baker, Mallinckrodt), used as received and stored over 3-Å molecular sieves. Ethanol was commercially available (Rossville Gold Shield), used as received, and stored over 3-Å molecular sieves. 2-Propanol was repackaged material, which was distilled. The fraction boiling at 82–83 °C was stored over 3-Å molecular seives. *tert*-Butyl alcohol was distilled from calcium hydride prior to use. Internal standards for GLC analysis were *n*-alkanes (Phillips).

Alkoxymercuration–Demercuration Procedures. Alkoxymercuration–demercuration procedures were carried out on scales ranging from ca. 0.7 to 5.0 mmol with the olefin and mercuric salt at 1 M concentration. The olefin was added via a calibrated syringe. After stirring the reaction mixtures for the desired period of time, demercuration was effected by adding a 200% excess of 3 M NaOH with vigorous stirring, followed by the addition of 0.5 M $NaBH_4$ in 3 M NaOH (100% excess in hydride). A known amount of an internal standard was added and the reaction mixture was extracted with *n*-pentane (reactions carried out in MeOH, EtOH, and *i*-PrOH) or *n*-hexane (in *t*-BuOH) so that the sum total concentration of all products (olefin, ethers, and alcohol) was ca. 1 M. The extracts were washed with an equal volume amount of water and then dried over anhydrous potassium carbonate. They were then subjected to GLC analysis. When ROM–DM's were carried out with mercuric methanesulfonate in ethanol and 2-propanol under these conditions, the alkoxymercurials precipitated out of solution. Consequently, these reactions were carried out at concentrations of 0.2 M. The remainder of the procedure was as previously described. Also, for ROM's carried out at 0 °C, the DM was also carried out at 0 °C.

GLC Analysis. GLC analysis was carried out on an F&M 500 gas chromatograph equipped with the following columns: (a) 6 ft × $^1/_4$ in. 15% DC 710 on 60/80 AW-DCMS Chromosorb W; (b) 12 ft (6 ft) × $^1/_4$ in. 20% Carbowax 20M on 60/80 AW-DCMS Chromosorb W; (c) 6 ft × $^1/_4$ in. 15% SE-30 on 60/80 AW-DCMS Chromosorb W. Product identification was based on spiking the reaction mixtures with pure samples. The ethers were identified by isolation and characterization from preparative-scale ROM–DM reactions. The alcohols were available from previous studies in these laboratories.

Spectral Properties of the Ethers. Infrared spectra were recorded on neat samples with a Perkin-Elmer 137 spectrophotometer. NMR spectra were recorded on samples dissolved in carbon tetrachloride (ca. 10% v/v), relative to tetramethylsilane, on a Varian T-60 spectrometer.

Cyclohexyl methyl ether: ^{1}H NMR (CCl_4) δ 3.23, 3.05 (s, m, shift determined by Eu(fod)$_3$, 4 H), 0.95–2.12 (m, 10 H); IR (neat) cm^{-1} 1370, 1111, 1093 (d, C–O).

Methyl α-phenethyl ether: ^{1}H NMR (CCl_4) δ 7.20 (s, 5 H), 4.15 (q, 7 Hz, 1 H), 3.12 (s, 3 H), 1.35 (d, 7 Hz, 3 H); IR (neat) cm^{-1} 1368, 1112 (C–O).

Methyl pinacolyl ether: ^{1}H NMR (CCl_4) δ 3.27 (s, 3 H), 282 (q, 6 Hz, 1 H), 1.00 (d, 6 Hz), 0.87 (s) 12 H total; IR (neat) cm^{-1} 1399, 1372, 1116 (C–O).

2-Hexyl methyl ether: ^{1}H NMR (CCl_4) δ 3.24, 3.23 (m, s, 4 H), 0.75–1.70 (m, 12 H); IR (neat) cm^{-1} 1376, 1129, 1104 (d, C–O).

Methyl *exo*-norbornyl ether: ^{1}H NMR (CCl_4) δ 3.20, 3.15 (m, s, 4 H), 2.25 (m, 2 H), 0.90–1.77 (m, 8 H); IR (neat) cm^{-1} 1366, 1105 (C–O).

Methyl thexyl ether: ^{1}H NMR (CCl_4) δ 3.12 (s, 3 H), 1.03 (s), 0.67–2.08 (AB_6 m) 13 H total; IR (neat) cm^{-1} 1164, 1095 (C–O).

***tert*-Amyl methyl ether**: ^{1}H NMR (CCl_4) δ 3.10 (s, 3 H), 1.07 (s), 0.67–2.00 (A_2B_3 m), 11 H total; IR (neat) cm^{-1} 1379, 1361, 1190 (C–O).

Cyclohexyl ethyl ether: ^{1}H NMR (CCl_4) δ 3.40, 3.17 (q, 7 Hz, overlapping m, shift determined by Eu(fod)$_3$, 3 H), 0.85–2.33, 1.13 (m, t, 7 Hz, 13 H); IR (neat) cm^{-1} 1379, 1368 (sh), 1109 (C–O).

Ethyl α-phenethyl ether: ^{1}H NMR (CCl_4) δ 7.18 (s, 5 H), 4.28 (q, 7 Hz, 1 H), 3.27 (q, 7 Hz, 2 H), 1.35 (d, 7 Hz, 3 H), 1.11 (t, 7 Hz, 3 H); IR (neat) cm^{-1} 1372, 1117 (C–O).

Ethyl pinacolyl ether: ^{1}H NMR (CCl_4) δ 3.60, 3.28 (OCH_2CH_3, AB of ABX_3, 9.0 Hz (gem), 7.0 Hz (vic)), 2.90 (q, 7.0 Hz) 3 H total, 1.12 (t, X_3 of ABX_3, 7.0 Hz), 1.00 (d, 7.0 Hz), 0.83 (s), 15 H total; IR (neat) cm^{-1} 1399, 1370, 1115 (C–O).

Ethyl 2-hexyl ether: ^{1}H NMR (CCl_4) δ 3.68, 3.38 (AB of ABX_3, J = 7.0, 8.8 Hz, overlapping m, 3 H), 1.00, 0.7–1.37 (t, 7.0 Hz, X_3 of ABX_3, m, 15 H); IR (neat) cm^{-1} 1376, 1121, 1095 (d, C–O).

Ethyl *exo*-norbornyl ether: ^{1}H NMR (CCl_4) δ 3.37 (q, 7 Hz, m, 3 H), 2.25 (m, 2 H) 1.12, 0.77–1.75 (t, 7 Hz, m, 11 H); IR (neat) cm^{-1} 1374, 1112 (C–O).

Ethyl thexyl ether: ^{1}H NMR (CCl_4) δ 3.30 (q, 7 Hz, 2 H), 1.42–2.00 (m, A of AB_6, 1 H), 1.10 (t, 7 Hz), 1.03 (s), 0.97 (d, B_6 of AB_6), 15 H total; IR (neat) cm^{-1} 1393, 1376, 1166, 1082 (C–O).

***tert*-Amyl ethyl ether**: ^{1}H NMR (CCl_4) δ 3.30 (q, 7 Hz, 2 H), 1.10, 0.73–1.35 (t, 7 Hz, A_2B_3 m, 14 H); IR (neat) cm^{-1} 1385, 1366, 1193, 1085 (C–O).

Cyclohexyl 2-propyl ether: ^{1}H NMR (CCl_4) δ 3.65, 3.25 (septet, 7 Hz, m, 2 H), 1.08, 0.95–2.15 (d, 7 Hz, m, 16 H); IR (neat) cm^{-1} 1387, 1373, 1134 or 1087 (C–O).

Isopropyl α-phenethyl ether: ^{1}H NMR (CCl_4) δ 7.20 (s, 5 H), 4.42 (q, 6.0 Hz, 1 H), 3.42 (septet, 6.0 Hz, 1 H), 1.33 (d, 6.0 Hz), 1.07 (d, 6.0 Hz, $OCHCH_3CH_3$), 1.00 (d, 6.0 Hz, $OCHCH_3CH_3$); IR (neat) cm^{-1} 1379, 1371, 1100 (C–O).

Isopropyl pinacolyl ether: ^{1}H NMR (CCl_4) δ 3.53 (septet, 6 Hz, 1 H), 3.00 (q, 6 Hz, 1 H), 1.10, 1.07, 0.98, 0.83 (d, d, d, all 6 Hz, s), 0.92 (s), 15 H total; IR (neat) cm^{-1} 1387, 1372, 1115, 1110 (C–O).

2-Hexyl isopropyl ether: ^{1}H NMR (CCl_4) δ 3.53 (septet, m, 2 H), 0.65–1.58 (m, 9 H); IR (neat) cm^{-1} 1377, 1111 (C–O).

Isopropyl *exo*-norbornyl ether: ^{1}H NMR (CCl_4) δ 3.53 (septet, 6 Hz, m, 2 H), 2.18 (m, 2 H), 1.07, 0.82–1.82 (d, 6 Hz, m) 14 H total; IR (neat) cm^{-1} 1382, 1371, 1135 (C–O).

Isopropyl thexyl ether: ^{1}H NMR (CCl_4) δ 3.73 (septet, 6 Hz, 1 H), 1.65 (A of AB_6, 1 H), 1.03, 1.02 (d, s, 18 H); IR (neat) cm^{-1} 1381, 1368, 1166, 1082 (C–O).

***tert*-Amyl isopropyl ether**: ^{1}H NMR (CCl_4) δ 3.69 (septet, 6.5 Hz, 1 H), 1.43 (m, A_2 of A_2B_3, 2 H), 1.23, 1.05, 0.85 (s, d, 6.5 Hz, B_3 of A_2B_3) 15 H total; IR (neat) cm^{-1} 1385, 1371, 1193 or 1127, 1024 (C–O).

3,3-Dimethylbutyl isopropyl ether: ^{1}H NMR (CCl_4) δ 3.43, 3.35 (septet, 6 H, t, 7 Hz, 3 H total), 1.42 (t, 7 Hz, 2 H), 1.08 (d, 6 Hz, 6 H), 0.92 (s, 9 H).

***tert*-Butyl cyclohexyl ether**: ^{1}H NMR (CCl_4) δ 3.25 (m, 1 H), 1.00–1.95 (m), 1.15 (s, *t*-Bu) 19 H total; IR (neat) cm^{-1} 1397, 1368 (*t*-Bu), 1202, 1079 (C–O).

***tert*-Butyl α-phenethyl ether**: ^{1}H NMR (CCl_4) δ 7.20 (s, 5 H), 4.73 (q, 7 Hz, 1 H), 1.30 (d, 7 Hz, 3 H), 1.12 (s, 9 H); IR (neat) cm^{-1} 1389, 1360 (*t*-Bu), 1205, 1092 (C–O).

***tert*-Butyl pinacolyl ether**: ^{1}H NMR (CCl_4) δ 3.23 (q, 6 Hz), 1.15 (s), 1.00 (d, 6 Hz), 0.83 (s).

***tert*-Butyl 2-hexyl ether**: ^{1}H NMR (CCl_4) δ 3.47 (m, 1 H), 0.67–1.60 (m, ~21 H), 1.13 (*t*-Bu); IR (neat) cm^{-1} 1473, 1391, 1370 (*t*-Bu), 1205, 1062 (C–O).

***tert*-Butyl *exo*-norbornyl ether**: ^{1}H NMR (CCl_4) δ 3.35 (m, *endo*-2, 1 H), 2.08 (m, bridgeheads, 2 H), 1.08–1.78, 1.12 (m, s, ~17 H); IR (neat) cm^{-1} 1387, 1359, (*t*-Bu), 1193, 1097 (C–O).

***tert*-Butyl 3,3-dimethylbutyl ether**: ^{1}H NMR (CCl_4) δ 3.33 (t, 7 Hz), 1.42 (t, 7 Hz), 1.13 (s), 0.92 (s).

Dicyclohexyl ether: ^{1}H NMR (CCl_4) δ 3.30 (m, 2 H), 0.90–2.23 (m, 20 H); IR (neat) cm^{-1} 1092 (C–O).

Registry No. $Hg(OAc)_2$, 1600-27-7; $Hg(TFA)_2$, 13257-51-7; $Hg(NO_3)_2$, 10045-94-0; $Hg(OMs)_2$, 54253-64-4; n-$C_4H_9CH{=}CH_2$, 592-41-6; $(CH_3)_3CCH{=}CH_2$, 558-37-2; $(CH_3)_2C{=}CHCH_3$, 513-35-9; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; CH_3OH, 67-56-1; CH_3CH_2OH, 64-17-5; $(CH_3)_2CHOH$, 67-63-0; $(CH_3)_3COH$, 75-65-0; styrene, 100-42-5; cyclohexene, 110-83-8; norbornene, 498-66-8; cyclohexyl methyl ether, 931-56-6; methyl α-phenethyl ether, 4013-34-7; methyl pinacolyl ether, 25246-75-7; 2-hexyl methyl ether, 25246-71-3; methyl *exo*-norbornyl ether, 31022-89-6; methyl thexyl ether, 26356-10-5; *tert*-amyl methyl ether, 994-05-8; cyclohexyl ethyl ether, 932-92-3; ethyl α-phenethyl ether, 3299-05-6; ethyl pinacolyl ether, 25246-76-8; ethyl 2-hexyl ether, 25246-72-4; ethyl *exo*-norbornyl ether, 25273-25-0; ethyl thexyl ether, 90367-80-9; *tert*-amyl ethyl ether, 919-94-8; cyclohexyl 2-propyl ether, 1860-29-3; isopropyl α-phenethyl ether, 65757-61-1; isopropyl pinacolyl ether, 25246-77-9; 2-hexyl isopropyl ether, 25246-73-5; isopropyl *exo*-norbornyl ether, 25273-26-1; isopropyl thexyl ether, 90367-81-0; *tert*-amyl isopropyl ether, 3249-46-5; 3,3-dimethylbutyl isopropyl ether, 90367-82-1; *tert*-butyl cyclohexyl ether, 25246-83-7; *tert*-butyl α-phenethyl ether, 90367-83-2; *tert*-butyl pinacolyl ether, 25246-78-0; *tert*-butyl 2-hexyl ether, 25246-74-6; *tert*-butyl *exo*-norbornyl ether, 25273-27-2; *tert*-butyl 3,3-dimethylbutyl ether, 4419-58-3; dicyclohexyl ether, 4645-15-2; *tert*-butyl 1-hexyl ether, 69775-79-7; 2-hexanol, 626-93-7; benzeneethanol, 60-12-8; 2-(*tert*-butoxy)-3,3-dimethylbutane, 25246-78-0; 3,3-dimethyl-1-butanol, 624-95-3; cyclohexanol, 108-93-0; 2,3-dimethyl-2-butanol, 594-60-5; *exo*-norborneol, 497-37-0; *exo*-norborneol acetate, 36914-56-4; 2-methyl-2-butanol, 75-85-4.