TABLE I

THE NEAT REACTIONS OF ACID HALIDES WITH ORGANOTIN HYDRIDES AT AMBIENT TEMPERATURES[a]

$$3RCOX + 3R'_3SnH \rightarrow RCHO + RCO_2CH_2R + 3R'_3SnX$$

	% yield					
	R' = CH_3		R' = *n*-Bu		R' = C_6H_5	
	Aldehyde	Ester	Aldehyde	Ester	Aldehyde	Ester
			RCOCl			
CH_3	15	85	5[b]	95[b]		
C_2H_5				87[b]	14[c]	50[c]
Me_2CHCH_2	10	90				
$C_6H_5CH_2$			55[b]	45[b]	6.6[c]	
C_6H_5				99[d,e]		99[f]
p-MeC_6H_4	*g*	99				
p-$MeOC_6H_4$	25	75				
m-$NO_2C_6H_4$	*g*	99				
			RCOBr			
CH_3	12	88	69	31		
C_2H_5	16	84	65	35		
Me_2CHCH_2	54	46	40	60		
C_6H_5	40	63[e]	97	*h*		
			RCOF			
C_6H_5	*g*	99[i]	*g*	99[i]		
$C_6H_5CH_2$			*g*	99[i]		

[a] Aldehyde yields were determined from the 2,4-dinitrophenyldhydrazone derivitive. The ester yields were ascertained by difference from theoretical and identified by infrared and glpc as the only other reduction product. [b] Reported yield.[2] [c] Reference 5. [d] We were unable to duplicate a previous result[3] of 65% benzaldehyde. [e] Yield based on isolation. [f] Reference 4. [g] None observed. [h] Trace. [i] 0.6 *M* benzene solution.

100° and weighed. The precipitate was then carefully recrystallized from an ethanol–ethyl acetate mixture and weighed again.

Isolation Experiment.—A 0.33-mol scale reduction of benzoyl bromide with triethyltin hydride in 250 ml of absolute ether was carried out. Fractional distillation of the reaction mixture gave a pure fraction of benzyl benzoate which amounted to a 63% yield. The yield of benzaldehyde by difference was 37%. A duplicate reaction which was run concurrently and analyzed by the 2,4-dinitrophenylhydrazine method gave a benzaldehyde yield of 43% before recrystallization.

The Influence of Silver Acetate on the Oxymercuration–Demercuration of Olefins

SUNG MOON AND BURTON H. WAXMAN

Department of Chemistry, Adelphi University, Garden City, New York 11530

Received August 7, 1968

The oxymercuration–demercuration reaction is a well-known method of preparation of alcohols from olefins.[1–3] Bordwell[4] has demonstrated that the cyclization of 4-cycloocten-1-ol is pH dependent. He has also demonstrated that the demercuration is pH dependent. However, no work has been done on the influence of metallic cations on the oxymercuration–demercuration reaction.

In an effort to study the competition of silver ion and mercuric ion for the exocyclic double bond of 4-vinylcyclohexene, a mercuric acetate solution was added to 4-vinylcyclohexene in tetrahydrofuran (THF) in the presence of silver acetate. After alkaline treatment with sodium borohydride, followed by extraction, the product was analyzed by gas chromatography. In addition to the expected alcohol, 4-acetylcyclohexene was obtained. The ketone/alcohol ratio was 2:3.

The oxymercuration–demercuration reaction in the presence of silver acetate was studied with various olefins (see Table I). The addition of the aqueous mercuric acetate solution to the THF–olefin–silver acetate mixture produced only a transitory yellow color which disappeared quickly. The reaction appeared to be at least as rapid as normal oxymercuration.

Demercuration must be preceded by the addition of base to the reaction mixture. When the demercuration was carried out without this step only the alcohol was obtained. The oxymercuration reaction is quantitative; however, the demercuration reaction results in a great deal of regenerated olefins. Consequently, the absolute yields of ketone as prepared by this method are poor. The reaction is useful to the extent that exocyclic double bonds are converted into ketones, while endocyclic double bonds are relatively inert, and the reaction conditions are mild enough to leave the most easily oxidized groups unaffected.

The realization that acyclic olefins yield a greater

---

(1) J. Chatt, *Chem. Rev.*, **48,** 7 (1951).

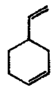
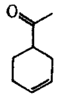
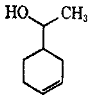
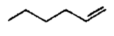
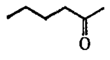
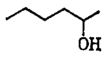
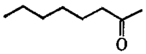
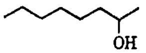
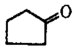
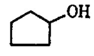
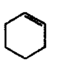
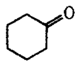
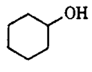
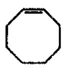
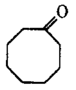
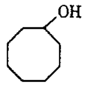
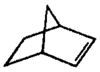
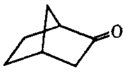
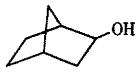
(2) N. S. Zefirov, *Russ. Chem. Rev.*, **34,** 527 (1965).

(3) W. Kitching, *Organometal. Chem. Rev.*, **3** (1), 61 (1968).

(4) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88,** 993 (1966).

TABLE I

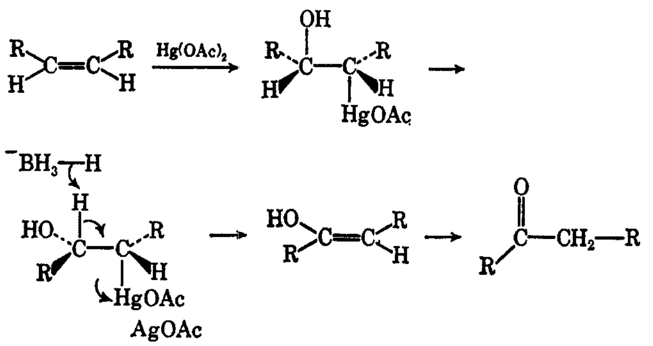
RATIO OF KETONE/ALCOHOL PRODUCED BY OXYMERCURATION-DEMERCURATION IN THE PRESENCE OF SILVER ACETATE

Olefin	Ratio of AgOAc/olefin	Ketone	Alcohol	Ratio of ketone/alcohol
	1.3:1			1:1.5
	1:1			6.5:1 (13:2%)
	1.2:1			3:1 (12:4%)
	1.45:1			9:1
	1.8:1			5.7:1
	1.45:1			1:1.5
	1.45:1			1:3
	1.2:1			1:2.7 (14:38%)
	1.45:1			6.5:1 (26:4%)
	1.8:1			(<1:>99%)

ratio of ketone to alcohol suggests a mechanism for the reaction.

The normal mode of oxymercuration of most of the olefins investigated (an exception being norbornene) is *trans*. It is reasonable to assume that oxymercuration in the presence of silver acetate would be the same. The demercuration reaction, however, may be a dehydromercuration which proceeds in an E2 manner (see Scheme I). It is obvious that the acyclic systems

SCHEME I



are capable of twisting to accommodate the required geometry, while the cyclic systems are not. The high ratio of ketone/alcohol in the case of cyclooctene compared with that of the other cyclic olefins attests to its greater flexibility. The absence of any ketone generated from norbornene might be an indication that the reaction is indeed a dehydromercuration. The norbornene system should be inert to dehydromercuration owing to the unavailability of its *endo* hydrogens and its inability to undergo a twist of even 30°.[5]

Of additional interest is the lack of ketone formed when silver nitrate is substituted for the silver acetate. No explanation is offered for this observation.

It should be noted that the true ratios of ketone/alcohol may be somewhat greater than those reported. The conditions for demercuration are also those conditions for reduction of the ketones to the alcohols. The alcohols thus formed are indistinguishable from normal oxymercuration-demercuration products. The exception is again norbornene where the reduction product of the corresponding ketone is the *endo* alcohol. However, no *endo* alcohol was observed. It should also be noted that, when silver acetate was added to the normal oxymercuration product prior to treatment with alkaline sodium borohydride, no ketone was formed.

Experimental Section[6]

Oxymercuration-Demercuration of 4-Vinylcyclohexene in the Presence of Silver Acetate.—4-Vinylcyclohexene (1.08 g, 0.01 mol) was added to a mixture of silver acetate (2.16 g, 0.013 mol) in a solution of 10 ml of water and 10 ml of THF. The mixture was stirred for 15 min at room temperature. A solution of 3.12 g of mercuric acetate (0.01 mol) in 10 ml of water was added slowly. A yellow suspension developed immediately but soon (30 sec) disappeared. The mixture was stirred for 0.5 hr at room temperature. A solution of 3 *M* NaOH (10 ml) was added, followed by 0.5 g of sodium borohydride in 10 ml of 3 *M* NaOH. The water layer was saturated with sodium chloride, and the product was extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and concen-

---

[5] T. G. Traylor, *J. Amer. Chem. Soc.*, **86**, 244 (1964).

[6] For gas chromatographic analysis, and F & M Model 720 gas chromatograph was used. The liquid phase absorbents employed were Carbowax 1540, silicone rubber (SE-30), 1,2,3-tris(cyanoethoxy)propane (TCEP), and ethylene glycol adipate (EGA). Infrared spectra were recorded with a Perkin-Elmer Infracord Model 337, and a Varian A-60 spectrometer was used to record the nmr spectra. The chemical shifts are shown in τ values from tetramethylsilane (TMS).

trated *in vacuo*. Gas chromatography (EGA at 83°) of the crude product showed two major peaks which were identified as methyl(4-cyclohexenyl) ketone (40%) and methyl(4-cyclohexenyl)carbinol (60%), by comparison of retention times on gas chromatography and ir spectra with those of authentic samples that were prepared as described below. No attempt to calculate absolute yield was made.

Preparation of Methyl(4-cyclohexenyl)carbinol.—Mercuric acetate (3.12 g, 0.01 mol) was dissolved in 10 ml of water. A 47% solution of boron trifluoride etherate (0.5 g, 0.0034 mol) was added followed by 10 ml of THF. 4-Vinylcyclohexene (1.2 g, 0.01 mol) was added and the yellow suspension disappeared in 15–20 sec. The solution was stirred overnight at room temperature and treated with sodium borohydride and recovered as above. Gas chromatography of the crude product (EGA at 83°) showed only one component: ir (CS_2) 3600, 3400, 3025 cm^{-1}; nmr (CCl_4) δ 4.4 (s, 2), 6.4 (m, 1), 6.9 (s, 1), 8.05 (m, 5) 8.5 (m, 2), 8.8 (d, 3). Based on spectral evidence, the structure was assigned as methyl(4-cyclohexenyl)carbinol.

Oxidation of Methyl(4-cyclohexenyl)carbinol.—The crude product of the boron trifluoride catalyzed oxymercuration–demercuration of 4-vinylcyclohexene was added to 20 ml of dry pyridine and 1.0 g of CrO_3. The mixture was stirred overnight at room temperature. The mixture was poured onto cracked ice and extracted with ether. The ethereal extract was washed with water, 3 *M* HCl, water, Na_2CO_3, and water, dried ($MgSO_4$), and concentrated by distillation. Gas chromatography (EGA at 83°) showed only one component which had a retention time somewhat less than that of the parent alcohol: ir (CS_2) 3025, 1710 cm^{-1}.

Oxymercuration–Demercuration of 1-Hexene in the Presence of Silver Acetate. A. Ratio of Silver Acetate/Olefin 1:1.—Silver acetate (1.66 g, 0.01 mol) was added to 20 ml of water. Mercuric acetate (3.12 g, 0.01 mol) was dissolved in 20 ml of water and added to the above mixture. THF (20 ml) was added and a yellow suspension developed. 1-Hexene (0.84 g, 0.01 mol) was added to the mixture. After 10 min no color change was evident. An additional 20 ml of THF was added and the color disappeared within 2 min. The mixture was stirred overnight at room temperature. A 3 *M* sodium hydroxide solution (10 ml) was added slowly, producing a brown precipitate. A solution of 1.0 g (0.027 mol) of sodium borohydride in 10 ml of 3 *M* NaOH was added slowly. The water layer was saturated with sodium chloride, and the product was extracted with 150 ml of ether. The ethereal extract was dried ($MgSO_4$) and concentrated by distillation. Gas chromatography (TCEP at 100°) showed two major peaks (beyond that of solvent and recovered olefin) which were identified as 2-hexanone (87%) and 2-hexanol (13%) by comparison of retention times and their infrared spectra with those of authentic samples. Cyclohexanone (0.3 g) was added as an internal standard, and the product yields were determined to be 2-hexanone (13%) and 2-hexanol (2%) by comparison of the peaks' areas.

B. Ratio of Silver Acetate/Olefin 1.2:1.—Silver acetate (2.0 g, 0.12 mol) was added to 10 ml of THF. 1-Hexene (0.84 g, 0.01 mol) was added and the mixture was stirred for 10 min. A solution of 3.5 g of mercuric acetate (0.011 mol) in 10 ml of water was added to the above mixture. A yellow suspension developed which cleared within 0.5 min. After 5 min the solution gave a negative test for mercuric ion. A solution of 3 *M* NaOH was added and a brown precipitate formed. The mixture was refluxed for 15 min and then cooled to room temperature. The mixture was cooled to ice–water temperature and treated with 0.7 g (0.019 mol) of sodium borohydride in 10 ml of 3 *M* NaOH. The aqueous solution was saturated with sodium chloride and extracted with ether. The ethereal extract was dried ($MgSO_4$) and concentrated under reduced pressure. Gas chromatography (EGA at 115°) showed two peaks which were identified as 2-hexanone (75%) and 2-hexanol (25%). Cyclohexanone (0.5 g) was added and absolute yields were determined by comparison of the peaks' areas: 12% 2-hexanone and 4% 2-hexanol.

C. Ratio of Silver Acetate/Olefin 1.45:1.—Silver acetate (2.4 g, 0.0145 mol) was added to 10 ml of THF. 1-Hexene (0.84 g, 0.01 mol) was added and the mixture was stirred at room temperature for 15 min. The mixture was treated with mercuric acetate and reduced, and the product was isolated as above. Gas chromatography of the crude product showed a ketone alcohol ratio of 9:1. No attempt was made to calculate absolute yields.

Oxymercuration–Demercuration of 1-Octene in the Presence of Silver Acetate.—Silver acetate (3.0 g, 0.018 mol) was added to 10 ml of THF. 1-Octene was added, followed by a solution of 3.12 g of mercuric acetate (0.01 mol) in 10 ml of water. The above procedure of sodium borohydride treatment and the product isolation was followed. Gas chromatography (EGA at 150°) showed the ketone/alcohol ratio to be 85:15. No attempt was made to calculate absolute yields.

Oxymercuration–Demercuration of Cyclopentene in the Presence of Silver Acetate. A. Nonalkaline Treatment with Sodium Borohydride.—Silver acetate (2.4 g, 0.0145 mol) was added to 15 ml of THF. Cyclopentene (0.72 g, 0.01 mol) was added, followed by a solution of 3.12 g of mercuric acetate (0.01 mol) in 20 ml of water. The mixture turned yellow, and the color disappeared within 20 sec. The reaction mixture was stirred for 15 min at room temperature. A solution of 0.325 g (0.0086 mol) of sodium borohydride in 10 ml of 3 *M* NaOH was added. The water layer was saturated with sodium chloride and the product was extracted with ether. The ethereal exrract was dried ($MgSO_4$) and concentrated. Gas chromatogtaphy (DEGS) at 40° showed no ketone present, only alcohol.

B. Alkaline Treatment with Sodium Borohydride.—The oxymercuration steps were identical with those above. NaOH (3 *M*, 20 ml) was added, followed by treatment with a solution of 0.4 g of sodium borohydride (0.011 mol) in 10 ml of 3 *M* NaOH. The product was isolated as described above. Gas chromatography (DEGS at 40°) showed the ketone/alcohol ratio to be 39:61. No attempt was made to calculate absolute yields.

Oxymercuration–Demercuration of Cyclohexene in the Presence of Silver Acetate.—The procedure was identical with that described immediately above. The ketone/alcohol ratio was found to be 25:75. No attempt was made to calculate absolute yields.

Oxymercuration–Demercuration of Cyclooctene in the Presence of Silver Acetate. A. Ratio of Silver Acetate/Olefin 1.2:1.—Silver acetate (2.0 g, 0.012 mol) was added to 10 ml of THF followed by 1.10 g of cyclooctene (0.01 mol). A solution of 3.12 g of mercuric acetate (0.01 mol) in 10 ml of water was added, producing a yellow color. The color did not disappear, and the mixture was stirred overnight at room temperature. After 18 hr the mixture was clear. A solution of 3 *M* NaOH (10 ml) was added, followed by 4 ml of a solution of 0.5 g of sodium borohydride in 10 ml of 3 *M* NaOH. The product was isolated as described above. Gas chromatography (EGA at 110°) showed the ketone/alcohol ratio to be 26:74. Cycloheptanone (0.5 g) was added as internal standard. The absolute yields, as calculated by integration of areas, were found to be 14% cyclooctanone and 39% cyclooctanol.

B. Ratio of Silver Acetate/Olefin 1.45:1.—Silver acetate (2.42 g, 0.0145 mol) was added to 15 ml of THF. Cyclooctene (1.12 g, 0.01 mol) was added, followed by a solution of 3.12 g of mercuric acetate (0.01 mol) in 10 ml of water. The yellow color did not completely disappear in 24 hr. The mixture was treated with 3 ml of 6 *M* NaOH, followed by a solution of 0.5 g of sodium borohydride in 10 ml of 3 *M* NaOH. The product was recovered as above. Gas chromatography of the product showed the ketone/alcohol ratio to be 84:16. Cyclohexanone (0.1 g) was added as internal standard. The absolute yields as calculated by integration of areas were found to be 26% cyclooctanone and 4% cyclooctanol.

Oxymercuration–Demercuration of Norbornene in the Presence of Silver Acetate.—Silver acetate (3.0 g, 0.018 mol) was added to 10 ml of THF, followed by 0.94 g of norbornene (0.01 mol) and a solution of 3.12 g of mercuric acetate in 10 ml of water. The mixture was stirred for 17 hr and then worked up as above. Gas chromatography of the product (EGA at 120°) showed only one peak. The product was collected by gas chromatography. Its ir spectrum was identical with that of an authentic sample of *exo*-norborneol.

Registry No.—Silver acetate, 563-63-3; 4-vinylcyclohexene, 100-40-3; methyl(4-cyclohexenyl)carbenol, 17264-01-6; 1-hexene, 592-41-6; 1-octene, 111-66-0; cyclopentene, 142-29-0; cyclooctene, 931-88-4; norbornene, 498-66-8; cyclohexene, 110-83-8.