= Br): yield 42%; mp 115–117 °C; IR (chloroform) 3410, 3220 cm^{-1} (NH stretch). Anal. Calcd for $C_8H_7BrN_4$: C, 40.19; H, 2.95. Found: C, 40.66; H, 3.12. **9** (Y = OCH_3): yield 35%; mp 99–101 °C; IR (chloroform) 3400, 3210 cm^{-1} (NH stretch). Anal. Calcd for $C_9H_{10}N_4O$: C, 56.83; H, 5.30. Found: C, 57.02; H, 5.40. **9** (Y = CH_3): yield 44%; from thin-layer chromatography of the mother liquor an additional 22% was obtained; melting range 100–104 °C; IR (chloroform) 3400, 3220 cm^{-1} (NH stretch). Anal. Calcd for $C_9H_{10}N_4$: C, 62.05; H, 5.79. Found: C, 62.23; H, 5.83.

Determination of the pK_a of 6-R^3-3-phenyl-1,6-dihydro-1,2,4,5-tetrazines 3a (R^3 = H), 3b (R^3 = CH_3), and 3c (R^3 = C_2H_5). Calculation of the pK_a of 2a. The pK_a was determined by UV spectroscopy.[23] Each compound was measured in seven buffer solutions of different pH,[24] in a buffer solution of pH 7.5 (neutral species), and in a buffer solution of pH 12.9 (conjugate base). A stock solution in 10 mL of ethanol was prepared from which 1 mL was added to the buffer solutions. The pK_a values are as follows: **3a**, 10.01 ± 0.03; **3b**, 9.77 ± 0.09; **3c**, 9.92 ± 0.08. UV data at pH 7.5: λ_{max} for **3a** 432 nm (log ϵ 2.93), 275 (4.05); for **3b** 431 (2.86), 275 (4.06); for **3c** 433 (2.91), 277 (4.08). UV data at pH 12.9: λ_{max} for **4a** 389 nm (log ϵ 3.28), 303 (4.15); for **4b** 385 (3.30), 303 (4.17); for **4c** 390 (3.26), 304 (4.17).

The pK_a value of **2a** was approximated by averaging the pK_a values of **3a–c**, which results in 9.90 ± 0.12.[25]

Acknowledgment. We are indebted to Mr. H. Jongejan for carrying out the microanalyses and to Drs. C. A. Landheer and Mr. W. P. Combé for mass spectrometric data.

Registry No. 1a, 36022-11-4; **1b**, 67131-36-6; **1c**, 78114-01-9; **2a**, 78199-51-6; **2b**, 78199-52-7; **2c**, 78199-53-8; **3a**, 76630-74-5; **3b**, 76630-75-6; **3c**, 76630-76-7; **3d**, 13717-81-2; **4a**, 76630-78-9; **4b**, 76630-79-0; **4c**, 76630-80-3; **4d**, 78199-54-9; **5a**, 76630-81-4; **5d**, 78199-55-0; **7** (Y = Br), 56107-99-4; **7** (Y = OCH_3), 56107-91-6; **7** (Y = CH_3), 37385-31-2; **8** (Y = Br), 72115-67-4; **8** (Y = OCH_3), 72115-80-1; **8** (Y = CH_3), 72115-68-5; **9** (Y = Br), 78199-56-1; **9** (Y = OCH_3), 78199-57-2; **9** (Y = CH_3), 78199-58-3; **10** (Y = Br), 78199-59-4; **10** (Y = OCH_3), 78199-60-7; **10** (Y = CH_3), 78199-61-8; **11** (Y = Br), 78199-62-9; **11** (Y = CH_3), 78199-63-0; **11** (Y = OCH_3), 78199-64-1; VIII (Y = H), 14418-30-5; 3,6-bis(*p*-methylphenyl)-1,2,4,5-tetrazine, 51973-26-3.

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(23) Albert, A.; Serjant, E. P. In "The Determination of Ionization Constants"; Chapman-Hall: London, 1971; Chapter 4.

(24) Buffer solutions according to: Sörensen, A. "Puffersubstanzen, Pufferlösungen, Puffer-Tritisole"; Merck A. G.: Darmstadt.

(25) The differences in σ_I for the geminal groups (H, CH_3, C_2H_5, and NH_2, Table II) are small; the Hammet equation, log $(k/k_o) = \rho\sigma$ or $-pK_X + pK_{NH_2} = \rho(\sigma_X - \sigma_{NH_2})$ predicts a difference of 0.06pK_a units (if $\rho = 1$) between **3c** and **2a**. This is below the experimental accuracy. Therefore the average value from **3a–c** was taken as the pK_a of **2a**: 9.90 ± 0.12.

Solvomercuration–Demercuration. 10. Oxymercuration–Demercuration of Olefins with the Mercuric Salts Acetate, Trifluoroacetate, Nitrate, and Methanesulfonate[1]

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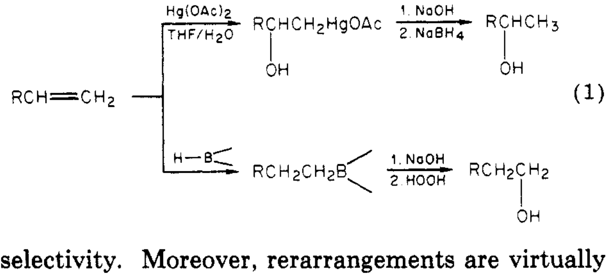
The oxymercuration–demercuration of a series of representative olefins has been examined with four mercuric salts: acetate, trifluoroacetate, nitrate, and methanesulfonate. Mono- and 1,2-disubstituted olefins undergo hydration with all four mercuric salts in 90–100% yields with a regioselectivity for the Markovnikov alcohol (from monoolefins) of ≥99.5%. Only styrene was found to be an exception. In marked contrast, only mercuric acetate is effective for the Markovnikov hydration of 1,1-di-, tri-, and tetrasubstituted olefins. The other three mercuric salts provide lower yields of the tertiary alcohols, yields which decrease rapidly with time. 1-Phenylcyclopentene undergoes only allylic oxidation with the mercuric salts trifluoroacetate, nitrate, and methanesulfonate. Mercuric acetate does give the normal hydration product but only in trace amounts. In this case, allylic oxidation is the major reaction pathway with this salt as well.

Introduction

The oxymercuration-demercuration (OM–DM) sequence with mercuric acetate in aqueous tetrahydrofuran is a valuable method for the Markovnikov hydration of olefins (eq 1). It is characterized by an exceptionally high regioselectivity. Moreover, rerarrangements are virtually unknown. Consequently, it nicely complements hydroboration–oxidation which leads to the anti-Markovnikov alcohols (eq 1).



(1)

Mercuric acetate is highly effective in this reaction.[2] However, looking to the future, we anticipated incorporating many nucleophiles other than water into the initial mercurial. (Hence, the series was entitled "Solvomercuration–Demercuration" rather than "Oxymercuration–Demercuration".) It appeared desirable to have definite information on the behavior of a series of mercuric salts with anions of decreasing nucleophilicity. Thus, it would be easy to shift to a more favorable salt when working with a solvent of greatly reduced nucleophilic properties.

There are several reports concerning the differing behavior of various mercuric salts.[3,4] While mercuric acetate

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(1) Solvomercuration–Demercuration. 9. Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 930.

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

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

Table I. Oxymercuration–Demercuration of Mono- and 1,2-Disubstituted Olefins

olefin	HgX_2	% alcohol[a] 15 min	% alcohol[a] 60 min
1-hexene	$Hg(OAc)_2$	94	95
	$Hg(TFA)_2$	92	93
	$Hg(NO_3)_2$	92	93
	$Hg(OMs)_2$	90	86
3,3-dimethyl-1-butene[f]	$Hg(OAc)_2$	88[b]	97[c]
	$Hg(TFA)_2$	97[d]	97[e]
	$Hg(NO_3)_2$	96	97
	$Hg(OMs)_2$	100	99
styrene	$Hg(OAc)_2$	92	96
	$Hg(TFA)_2$	67	56
	$Hg(NO_3)_2$	82	78
	$Hg(OMs)_2$	83	78
cyclohexene	$Hg(OAc)_2$	96	95
	$Hg(TFA)_2$	94	86
	$Hg(NO_3)_2$	99	98
	$Hg(OMs)_2$	88	91
norbornene	$Hg(OAc)_2$	85[g]	87[g]
	$Hg(TFA)_2$	95	95
	$Hg(NO_3)_2$	100	99
	$Hg(OMs)_2$	90	94

[a] Alcohols are Markovinkov unless otherwise noted. [b] 0.6% primary alcohol was observed. [c] 0.3% primary alcohol. [d] 0.5% primary alcohol. [e] 0.2% primary alcohol. [f] In a previous study (ref 2), the yield of primary alcohol was incorrectly reported as 3% with mercuric acetate. [g] A 15% yield of *exo*-norbornyl acetate was observed.

Table II. Oxymercuration–Demercuration of 1,1-Di-, Tri-, and Tetrasubstituted Olefins

olefin	HgX_2	% alcohol 15 min	% alcohol 60 min
2-methyl-1-pentene	$Hg(OAc)_2$	94	91
	$Hg(TFA)_2$	84	54
	$Hg(NO_3)_2$	55	3
	$Hg(OMs)_2$	60	32
2-methyl-2-butene	$Hg(OAc)_2$	94	95
	$Hg(TFA)_2$	88	43
	$Hg(NO_3)_2$	48	15
	$Hg(OMs)_2$	31	13
2,3-dimethyl-2-butene	$Hg(OAc)_2$	85	62
	$Hg(TFA)_2$	9	trace
	$Hg(NO_3)_2$	0	0
	$Hg(OMs)_2$	0	0

Table III. Oxymercuration–Demercuration of 1-Phenylcyclopentene

HgX_2	time, min	% products: tert alcohol[a]	% products: allylic alcohol[b]	% products: olefin
$Hg(OAc)_2$	15–60	trace	0	98
	1440	trace	35	53
$Hg(TFA)_2$	15	0	38	59
	60	0	41	56
	1440	0	46	37
$Hg(NO_3)_2$	15	0	36	57
	50	0	44	50
	1440	0	40	34
$Hg(OMs)_2$	15	0	18	79
	60	0	36	60
	1440	0	48	43

[a] 1-Phenylcyclopentanol. [b] 2-Phenylcyclopenten-3-ol.

and nitrate react readily with olefins to yield the expected oxymercurial, mercuric sulfate reacts to give a precipitate of unknown structure. On the other hand, the more covalent mercuric salts, such as the chloride and thiocyanate, are observed to react very slowly or not at all. To date, only mercuric acetate has been examined in the OM–DM of olefins in aqueous tetrahydrofuran.[2] Consequently, we undertook to examine further the OM–DM sequence with the mercuric salts, trifluoroacetate (TFA), nitrate, and methanesulfonate, and to compare them to mercuric acetate.[5] It appeared that the anions involved, acetate, trifluoroacetate, nitrate, and methanesulfonate, would provide a desirable range of decreasing nucleophilic properties.

These four mercuric salts possess significantly different characteristics. The gegenions are significantly different in their ability to compete with water for capture of the β-mercurated cationic intermediate. Their degrees of dissociation are also different. Moreover, the oxymercuration reaction generates 1 equiv of acid and this can affect the stability of the oxymercurials with time. Therefore, it became of interest to examine these four mercuric salts to determine what the effects of their differing properties would have on the overall hydration sequence.

Results and Discussion

The olefins investigated and the results are summarized in Tables I, II, and III.

Mono- and 1,2-Disubstituted Olefins. In general, these olefins undergo satisfactory hydration in yields of 90–100% with all four mercuric salts. High regioselectivity (>99.5%) for the Markovnikov product is observed with all of the monosubstituted olefins. Styrene, however, exhibits somewhat different behavior. Mercuric acetate results in virtually quantitative yields of α-phenethyl alcohol. On the other hand, the other three salts give significantly lower yields, along with a gummy polymeric substance. We assumed this to be polystyrene and did not investigate it further.

The OM–DM of norbornene with mercuric trifluoroacetate, the nitrate, and the methanesulfonate gives nearly quantitative yields of *exo*-norbornanol. With mercuric acetate, 85–87% yields of the alcohol are obtained along with a 15% yield of *exo*-norbornyl acetate. However, by using methanol as a cosolvent during the demercuration step, the ester is hydrolyzed and nearly quantitative yield of the alcohol is obtained.

1,1-Di-, Tri-, and Tetrasubstituted Olefins. An earlier examination of these olefins showed that with mercuric acetate sterically unhindered 1,1-di- and trisubstituted olefins are hydrated to give the tertiary alcohols in yields of greater than 90%. Moreover, these yields are constant with time. On the other hand, 2,3-dimethyl-2-butene is hydrated in lower yields which decrease rapidly with time.[2]

In marked contrast, the OM–DM of all of these olefins with mercuric trifluoroacetate, the nitrate, and the methanesulfonate gives significantly lower yields of the tertiary alcohols. The yields decrease with time—in some cases dropping to zero in just 1 h at room temperature.[1] We believe that the strong acid liberated from these salts during the oxymercuration step is at least partly responsible for this phenomenon. In one case, the OM–DM of 2-methyl-2-butene with mercuric nitrate was repeated, but 1 equiv of triethylamine was introduced. The yield of alcohol after 15 min was higher, 77%, and dropped only moderately to 68% in 1 h. This compares to yields of 48%

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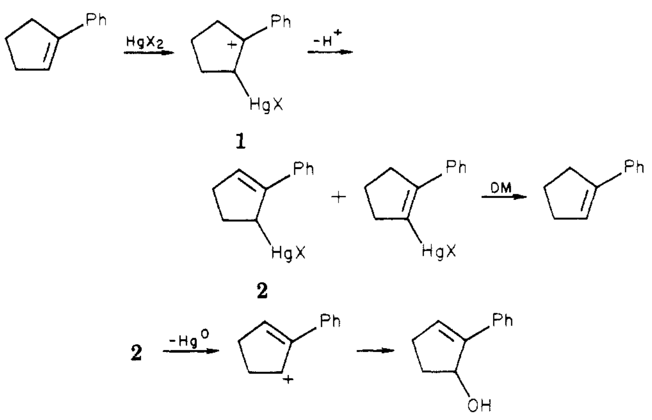
(4) Kitching, W. *Organometal. Chem. Rev.* **1968**, *3*, 51.

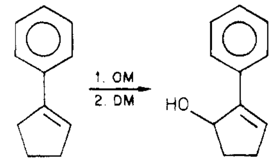
(5) A similar study in selected alcohol solvents with these mercuric salts has been undertaken. The results will be described in a future paper.

Scheme I



and 15% in the absence of the amine.

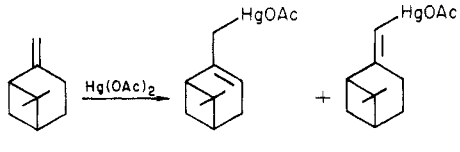
1-Phenylcyclopentene. In the previous investigation with mercuric acetate, this olefin was shown to be remarkably inert. Indeed, over 4 h very little oxymercuration was observed. However, longer reaction times resulted in significant reaction. But the expected Markovnikov product, the tertiary alcohol, is formed in only trace amounts. This product is not produced in the reaction with the other three mercuric salts examined in the present study. In these cases the major product is the allylic alcohol, 2-phenylcyclopenten-3-ol (eq 2), produced in a matter of minutes.



(2)

Allylic oxidation of olefins with mercuric salts are, of course, well-known, as examplified by the Denigès[6] and Treibs[7] reactions. However, they are usually carried out at relatively high temperatures with long reaction times of up to several hours.[8]

These results are readily explained by the proposed mechanism (Scheme I). For steric and/or electronic reasons, the initially formed intermediate (1) is resistant to nucleophilic capture. Instead, it eliminates a proton in either of two directions to form an allylic (2) and a vinyl mercurial. Allylic mercurials are well-known to undergo a facile solvolysis reaction, resulting in allylic ions. Previously, Coxon and co-workers[9] showed that the OM of β-pinene with mercuric acetate failed to give the expected oxymercurials but formed instead a mixture of the allylic and vinylic mercurial (eq 3).



(3)

Conclusion

The hydration of mono- and 1,2-disubstituted olefins can be effected by mercuric acetate, trifluoroacetate, nitrate, and methanesulfonate. The yields of alcohols are usually 90–100% and the regioselectivity for the Markovnikov product is extraordinarily high, ≥99.5%. Styrene appears to be an exception.

On the other hand, only mercuric acetate is effective for the hydration of 1,1-di-, tri-, and tetrasubstituted olefins. The other three salts give lower yields which decrease with time.

In contrast to the other trisubstituted olefins examined, 1-phenylcyclopentene undergoes virtually exclusive allylic oxidation as opposed to the normal oxymercuration.

Experimental Section

Materials. Tetrahydrofuran (Baker Analyzed Reagent), mercuric acetate, mercuric nitrate, mercuric oxide (all Mallinckrodt reagent), and methanesulfonic acid (Aldrich) were all used as received. Trifluoroacetic acid (3M Co.) and styrene (Baker Reagent) were distilled before use. 1-Hexene, 2-methyl-2-butene, and 2-methyl-1-pentene were Phillips Petroleum Co. products (99 mol %), used as received and stored over nitrogen. 3,3-Dimethyl-1-butene (Chemical Samples Co.), cyclohexene (Baker Reagent), and norbornene (Aldrich Chemical Co.) were used as received. Mercuric trifluoroacetate, mercuric methanesulfonate, and 1-phenylcyclopentene were prepared as described below.

Mercuric Trifluoroacetate. This compound was synthesized by the reaction of mercuric oxide (0.5 mol) and trifluoroacetic acid (2.0 mol). While the initial reaction was exothermic, heating was required to convert the last traces of mercuric oxide. Water and excess acid was removed by distillation under vacuum (0.2 mm), using an oil bath (maximum temperature, 120 °C), until the weight of the contents of the distillation flask were constant: 212.55 g. The resulting white solid exhibited a melting point of 165–168 °C (lit.[10] mp 167–169 °C).

Mercuric Methanesulfonate. This compound was prepared by the reaction of mercuric oxide (0.5 mol) and methanesulfonic acid (1.0 mol) in water (50 g). Again, the initial reaction was exothermic, but heating was required to obtain complete reaction of the mercuric oxide. Excess water was removed by distillation under vacuum to constant weight. Elemental analyses for C, H, and Hg were satisfactory.

1-Phenylcyclopentene. This olefin was prepared in 80% yield by the reaction of phenylmagnesium bromide and cyclopentanone, followed by refluxing in aqueous oxalic acid. This compound boiled at 70–74 °C (1.5 mm) [lit.[10] bp 72–74 °C (1.5 mm)].

General Procedure for the Oxymercuration–Demercuration Reaction. To a stirred mixture of 5.0 cm^3 of water, 5.0 cm^3 of tetrahydrofuran, and 5.0 mmol of the desired mercuric salt was added 5.0 mmol of olefin. After stirring for the desired length of time at room temperature, 5.0 cc of 3 M NaOH was added followed by 5.0 mmol of 0.5 M NaOH. The reaction mixture was saturated (K_2CO_3) and an appropriate internal standard was added. An aliquot was dried (K_2CO_3) and analyzed by VPC on a 12 ft × $^1/_4$ in. 10% Carbowax 20M or 12 ft x $^1/_4$ in. 15% DC 710 column.

Alcohol products were identified by comparison of VPC retention times with those of authentic samples of the alcohols.[2] In some cases (3,3-dimethyl-1-butanol, 2-methyl-2-pentanol, and 2-phenylcyclopenten-3-ol), the products were isolated from preparative scale reactions and identified by spectral data.

Results for 1-hexene, 3,3-dimethyl-1-butene, styrene, cyclohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene with mercuric acetate were reported in a previous publication.[2] Those reactions were all repeated for this study, and the results are reported in Tables I and II. There are some differences between the data reported here and in the earlier paper. However, they are within the limits of experimental error.

Registry No. 1-Hexene, 592-41-6; 3,3-dimethyl-1-butene, 558-37-2; styrene, 100-42-5; cyclohexene, 110-83-8; norbornene, 498-66-8; 2-methyl-1-pentene, 763-29-1; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; 1-phenylcyclopentene, 825-54-7; mercuric oxide, 15829-53-5; trifluoroacetic acid, 76-05-1; methanesulfonic acid, 75-75-2; phenyl bromide, 108-86-1; cyclopentanone, 120-92-3; $Hg(OAc)_2$, 1600-27-7; $Hg(TFA)_2$, 13257-51-7; $Hg(NO_3)_2$, 10045-94-0; $H(OMS)_2$, 54253-64-4.

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(6) Denigès, G. *Compt. Rend.* **1898**, *126*, 1043, 1145, 1868.

(7) Treibs, W. *Nature* **1948**, *35*, 125.

(8) Allylic oxidations of olefins by mercuric salts have been previously reviewed: Arzomanian, H.; Metzger, J. *Synthesis* **1971**, 527.

(9) Coxon, J. M.; Hartshorn, M. P.; Lewis, A. J. *Tetrahedron* **1970**, *26*, 3755.

(10) Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1969**, *91*, 5646.

(11) Garbisch, E. W., Jr. *J. Org. Chem.* **1961**, *26*, 4165.