

Aminomercuration of Olefins

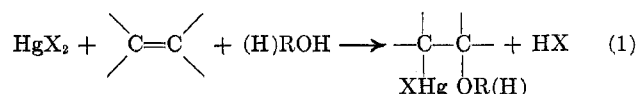
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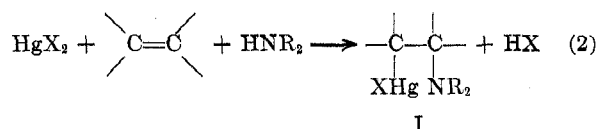
Olefins containing carbonyl, alcohol, or ether groups in the γ position to the double bond undergo facile addition of amine and HgCl residues (aminomercuration). The mechanism is thought to involve a cyclic transition state, wherein the mercury atom is held in position over the double bond to facilitate reaction.

The reaction of mercuric salts with olefins has been studied widely.¹⁻³ The majority of these studies center around oxymercuration in which either an alkoxy, carboxylate, or a hydroxyl group is added across a double bond along with a mercuric salt (eq 1). These



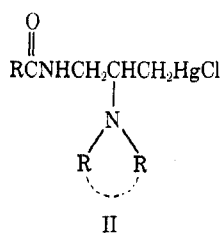
reactions are usually carried out in aqueous or alcoholic media and the solvent participates in the addition.

However, much less attention has been devoted to aminomercuration in which the elements of an amine (usually secondary) and a mercuric salt are added to a double bond (eq 2).



A few reports of this type of reaction in the literature⁴⁻⁸ have centered around the reactions of the olefins ethylene and styrene.

In 1957, Wendt and coworkers⁹ showed that various substituted allylureas would undergo aminomercuration to form derivatives possessing the general structure II.

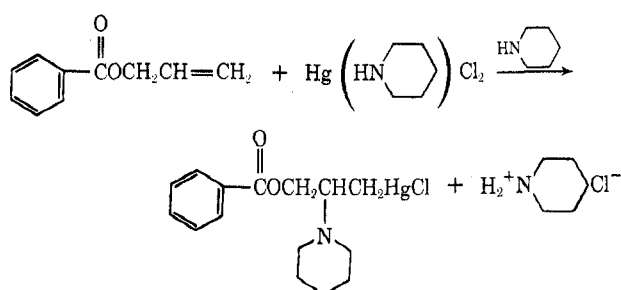


Only a few organomercurials possessing the structure of I and II have been reported; so we felt that more investigation in this area was necessary. Since the compounds reported by Wendt were formed quite well and were structurally more complicated than ethylene, we were led to believe that perhaps aminomercuration may be assisted by olefins which possess internal coordinating groups.

- (1) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).
- (2) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).
- (3) L. Makorova and A. Nesmeyanov, "Methods of Elemento-Organic Chemistry," Vol. 4, North-Holland Publishing Co., Amsterdam, 1967.
- (4) R. Kochetkova and R. Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 128 (1945).
- (5) R. Kochetkova, R. Freidlina, and A. Nesmeyanov, *Chem. Abstr.*, **42**, 1572 (1948).
- (6) A. Lattes and J. Périé, *C. R. Acad. Sci.*, 262, 1591 (1966).
- (7) G. Sach, *J. Chem. Soc.*, 733 (1949).
- (8) J. Périé and A. Lattes, *Bull. Soc. Chim. Fr.*, 583 (1970).
- (9) G. Wendt, B. Shetty, and W. Bruce, *J. Amer. Chem. Soc.*, **81**, 4233 (1959).

Results

Allylic Esters.—We have found that functionally substituted allyl derivatives react very well in aminomercuration. For example, allyl benzoate was found to react with a mercuric chloride-piperidine complex to give an addition product in 65% yield. Other addi-

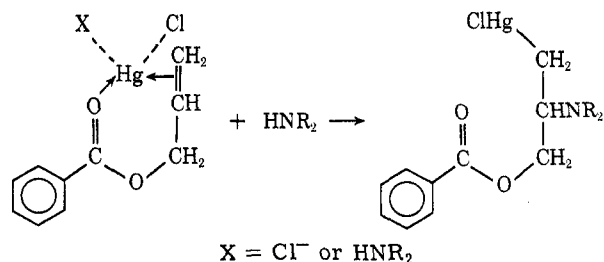


tion products of carbonyl-containing olefins with piperidine are summarized in Table I.

Typically, the addition is achieved by stirring equimolar amounts of the olefin and the mercuric chloride-amine complex in excess amine (solvent) for 1-3 days. The amine hydrochloride is filtered and the solvent is removed under vacuum. The addition product is then crystallized from ethanol. Stirring mercuric chloride and the olefin in piperidine worked equally well, but the reaction times were much longer due to difficulties in stirring heavy precipitates of mercuric chloride-amine complexes.

Aminomercuration is not limited to piperidine; other amines were found to yield addition products. The reaction products with allyl benzoate are listed in Table II. It is interesting to note that from the 2:1 complexes of amine with mercuric chloride, we were unable to form addition products with allyl benzoate.

We have found some restraints as to the structure of carbonyl-containing olefins which will undergo the aminomercuration reaction. The most favorable geometry involves mercuric ion and six other atoms which may form a seven-membered ring in the transition state.



The importance of carbonyl coordination is supported by the fact that electron-donating para-substituted

TABLE I
AMINOMERCURATION ADDUCTS FROM CARBONYL-CONTAINING OLEFINS WITH PIPERIDINE

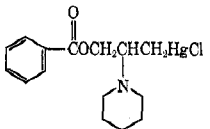
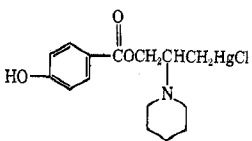
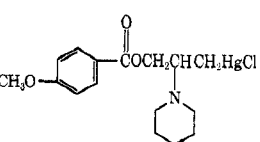
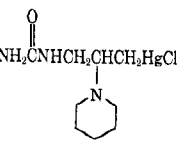
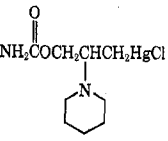
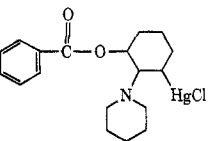
Olefin	HgCl ₂ -piperidine adduct	No.	Yield, %	Mp, °C	Recrystn solvent	Nmr, δ	Ir. cm ⁻¹	Anal.
Allyl		1	65	115-116	Absolute ethanol	(CDCl ₃) 8.0-8.2 (doublet, 2 H, <i>J</i> = 8 Hz, phenyl) and 7.4-7.6 (multiplet, 3 H, phenyl), 4.2-4.6 (octet, 2 H, <i>J</i> = 4 Hz, CH ₂ O), 3.1-3.4 (multiplet, 1 H, CHN), 2.5-3.0 (multiplet, 4 H, CH ₂ N), 2.2-2.3 (doublet, 2 H, <i>J</i> = 8 Hz, CH ₂ Hg), 1.4-1.8 (multiplet, 6 H, CH ₂)	(KBr) 2900 (CH), 1680 (C=O), 1260 (CO), 1120, 1030, 970, 710	Calcd for C ₁₅ H ₂₀ NO ₂ HgCl: C, 37.42; H, 4.16; N, 2.90; Cl, 7.40. Found: C, 37.37; H, 4.25; N, 2.80; Cl, 7.60.
Allyl <i>p</i> -hydroxybenzoate		2	14	122-123	Methanol	(DMSO- <i>d</i> ₆) 7.8-7.9 (doublet, 2 H, <i>J</i> = 8 Hz, phenyl) and 6.8-6.9 (doublet, 2 H, <i>J</i> = 8 Hz, phenyl), 4.1-4.5 (octet, 2 H, <i>J</i> = 4 Hz, CH ₂ O), 3.1-3.3 (multiplet, 1 H, CHN), 2.4-2.8 (multiplet, 4 H, CH ₂ N), 1.9-2.1 (doublet, 2 H, <i>J</i> = 8 Hz, CH ₂ Hg), 1.4-1.7 (multiplet, 6 H, CH ₂)	(KBr) 3350 (OH), 2930 (CH), 1680 (C=O), 1260 (CO), 1165, 850, 770	Calcd for C ₁₅ H ₂₀ NO ₂ HgCl: C, 36.21; H, 4.02; N, 2.89; Hg, 40.24; Cl, 7.05. Found: C, 35.99; H, 4.08; N, 3.06; Hg, 40.01; Cl, 7.12.
Allyl <i>p</i> -methoxybenzoate		3	40	97-98	Absolute ethanol	(CDCl ₃) 7.9-8.1 (doublet, 2 H, <i>J</i> = 8 Hz, phenyl) and 6.8-7.0 (doublet, 2 H, <i>J</i> = 8 Hz, phenyl), 4.1-4.6 (octet, 2 H, <i>J</i> = 4 Hz, CH ₂ O), 3.8 (singlet, 3 H, OCH ₃), 3.1-3.4 (multiplet, 1 H, CHN), 2.5-2.9 (multiplet, 4 H, CH ₂ N), 2.3-2.4 (doublet, 2 H, <i>J</i> = 8 Hz, CH ₂ Hg), 1.4-1.7 (multiplet, 6 H, CH ₂)	(KBr) 2900 (CH), 1695 (C=O), 1250 (CO), 1100, 1025, 840, 770	Calcd for C ₁₆ H ₂₂ NO ₂ HgCl: C, 37.57; H, 4.30; N, 2.74; Hg, 39.13; Cl, 6.85. Found: C, 37.32; H, 4.26; N, 2.71; Hg, 38.93; Cl, 6.59.
Allylurea		4	50	115-116	Ethyl acetate-isopropyl alcohol	(DMSO- <i>d</i> ₆) 6.1-6.4 (multiplet, 1 H, NH), 5.8-6.0 (multiplet, 2 H, NH ₂), 3.7-3.9 (multiplet, 2 H, CH ₂ NH), 3.2-3.6 (multiplet, 1 H, CHN), 2.8-3.0 (multiplet, 4 H, CH ₂ N), 2.2-2.4 (doublet, 2 H, <i>J</i> = 8 Hz, CH ₂ Hg), 1.7-2.0 (multiplet, 6 H, CH ₂)	(KBr) 3350 (NH), 3100 (NH), 1600 (C=O), 1270, 1190, 1070, 880, 855	Calcd for C ₉ H ₁₃ N ₃ OHgCl: C, 23.96; H, 4.40; N, 10.26; Hg, 48.90; Cl, 8.90. Found: C, 24.22; H, 4.19; N, 9.97; Hg, 48.75; Cl, 9.05.
Allyl carbanate		5	42	92-93	Isopropyl alcohol	(DMSO- <i>d</i> ₆) 6.3-6.5 (singlet, 2 H, NH ₂), 2.9-3.2 (multiplet, 1 H, CHN), 2.5-2.8 (multiplet, 4 H, CH ₂ N), 1.9-2.0 (doublet, 2 H, <i>J</i> = 8 Hz, CH ₂ Hg), 1.3-1.6 (multiplet, 6 H, CH ₂)	(KBr) 3300 (NH ₂), 2900 (CH), 1650 (C=O), 1440, 1100, 1050, 860, 750	Calcd for C ₉ H ₁₇ N ₂ O ₂ HgCl: C, 23.90; H, 4.14; N, 6.83; Hg, 48.78; Cl, 8.53. Found: C, 23.73; H, 4.01; N, 6.45; Hg, 48.89; Cl, 8.02.
3-Cyclohexenyl benzoate		6	6	133	Absolute ethanol	(CDCl ₃) 8.0-8.2 (doublet, 2 H, <i>J</i> = 8 Hz, phenyl) and 7.4-7.6 (multiplet, 3 H, phenyl), 5.6-5.7 (multiplet, 1 H, CHO), 2.9-3.1 (multiplet, 1 H, CHN), 2.6-2.8 (multiplet, 2 H, CH ₂ N), 2.0-2.2 (doublet, 2 H, <i>J</i> = 12 Hz, CH ₂ Hg), 1.4-1.8 (multiplet, 12 H, CH ₂)	(KBr) 2920 (CH), 1690 (C=O), 1440, 1275 (C-O), 1110, 880, 715	Calcd for C ₁₃ H ₂₁ NO ₂ HgCl: C, 41.45; H, 4.60; N, 2.68; Hg, 38.38; Cl, 6.71. Found: C, 41.25; H, 4.66; N, 2.66; Hg, 38.36; Cl, 6.50.

TABLE I
(Continued)

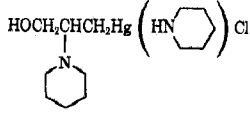
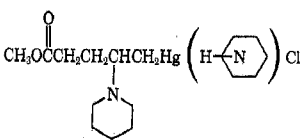
Olefin	HgCl ₂ -piperidine adduct	No.	Yield, %	Mp, °C	Recrystn solvent	Nmr, δ	Ir, cm ⁻¹	Anal.
Allyl acetate		7	74	67-68		Same as that obtained from allyl alcohol		
Methyl allylacetate		8	73	Oil		(CDCl ₃) 5.0 (singlet, 1 H, N-H), 3.6 (singlet, 3 H, OCH ₃), 2.8-3.2 (multiplet, 5 H, CH ₂ -NH ₂), 2.4-2.6 (multiplet, 4 H, CH ₂ N), 2.3-2.4 (multiplet, 2 H, CH ₂ C=O), 2.1-2.3 (doublet, 2 H, J = 8 Hz, CH ₂ Hg), 1.3-1.9 (multiplet, 12 H, CH ₂)		

TABLE II
AMINOMERCURATION ADDUCTS FROM ALLYL BENZOATE WITH VARIOUS AMINES^a

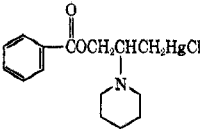
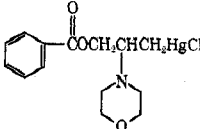
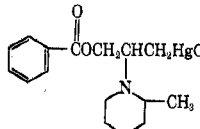
Amine	HgCl ₂ -allyl benzoate adduct	No.	Yield, %	Mp, °C	Recrystn solvent	Nmr, δ	Ir, cm ⁻¹	Anal.
Piperidine		1	65	115-116	Absolute ethanol	(CDCl ₃) 8.0-8.2 (doublet, 2 H, J = 8 Hz, phenyl) and 7.4-7.6 (multiplet, 3 H, phenyl), 4.2-4.6 (octet, 2 H, J = 4 Hz, CH ₂ O), 3.1-3.4 (multiplet, 1 H, CHN), 2.5-3.0 (multiplet, 4 H, CH ₂ N), 2.2-2.3 (doublet, 2 H, J = 8 Hz, CH ₂ Hg), 1.4-1.8 (multiplet, 6 H, CH ₂)	(KBr) 2900 (CH), 1680 (C=O), 1120, 1030, 970, 710	Calcd for C ₁₅ H ₂₀ NO ₂ HgCl: C, 37.42; H, 4.16; N, 2.90; Cl, 7.40. Found: C, 37.37; H, 4.25; N, 2.80; Cl, 7.60.
Morpholine		9	45	104	Absolute ethanol	(CDCl ₃) 8.0-8.2 (doublet, 2 H, J = 8 Hz, phenyl) and 7.4-7.6 (multiplet, 3 H, phenyl), 4.2-4.6 (octet, 2 H, J = 4 Hz, CH ₂ O), 3.6-3.9 (triplet, 4 H, J = 4 Hz, CH ₂ O), 3.1-3.4 (multiplet, 1 H, CHN), 2.6-2.9 (quartet, 4 H, J = 4 Hz, CH ₂ N), 2.2-2.3 (doublet, 2 H, J = 8 Hz, CH ₂ Hg)	(KBr) 2940 (CH), 2840 (CH), 1700 (C=O), 1440, 1250 (C-O), 1110, 850, 710	Calcd for C ₁₄ H ₁₅ NO ₂ HgCl: C, 34.78; H, 3.72; N, 2.90; Hg, 41.40; Cl, 7.24. Found: C, 34.56; H, 3.75; N, 2.84; Hg, 41.21; Cl, 7.28.
Hexamethyleneimine		10	26	108	Absolute ethanol	(CDCl ₃) 7.9-8.1 (doublet, 2 H, J = 8 Hz, phenyl), 7.4-7.6 (multiplet, 3 H, phenyl), 4.1-4.6 (octet, 2 H, J = 8 Hz, CH ₂ O), 3.1-3.4 (multiplet, 1 H, CHN), 2.7-3.0 (multiplet, 4 H, CH ₂ N), 2.2-2.4 (doublet, 2 H, J = 8 Hz, CH ₂ Hg), 1.5-1.8 (multiplet, 8 H, CH ₂)	(KBr) 2920 (CH), 1700 (C=O), 1450, 1280 (CO), 1130, 1070, 1030, 710	Calcd for C ₁₅ H ₂₂ NO ₂ HgCl: C, 38.78; H, 4.44; N, 2.82; Hg, 40.40; Cl, 7.07. Found: C, 38.69; H, 4.30; N, 2.70; Hg, 40.10; Cl, 7.00.

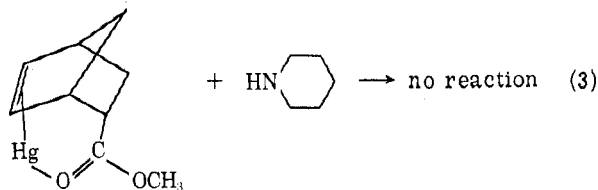
TABLE II
(Continued)

Amine	HgCl ₂ -allyl benzoate adduct	No.	Yield, %	Mp, °C	Recrystn solvent	Nmr, δ	Ir, cm ⁻¹	Anal.
4-Methyl-piperidine		11	27	104	Absolute ethanol	(CDCl ₃) 8.0-8.2 (doublet, 2 H, $J = 8$ Hz, phenyl) and 7.3-7.6 (multiplet, 3 H, phenyl), 4.2-4.6 (octet, 2 H, $J = 4$ Hz, CH ₂ O), 3.2-3.4 (multiplet, 1 H, CHN), 2.2-2.4 (doublet, 2 H, $J = 8$ Hz, CH ₂ -Hg), 1.1-1.8 (multiplet, 5 H, CH ₂ CH), 0.8-1.0 (doublet, 3 H, $J = 6$ Hz, CH ₃)	(KBr) 2900 (CH), 1700 (C=O), 1430, 1250 (CO), 1080, 710	Calcd for C ₁₈ H ₂₂ NO ₂ HgCl: C, 38.78; H, 4.44; N, 2.82; Hg, 40.40; Cl, 7.07. Found: C, 39.38; H, 4.60; N, 2.87; Hg, 41.25; Cl, 7.08.
2-Methyl-piperidine		12	6	127	Absolute ethanol	(CDCl ₃) 8.0-8.1 (doublet, 2 H, $J = 8$ Hz, phenyl) and 7.3-7.6 (multiplet, 3 H, phenyl), 4.1-4.6 (octet, 2 H, $J = 4$ Hz, CH ₂ O), 2.8-3.1 (multiplet, 1 H, CHN), 2.3-2.5 (doublet, 2 H, $J = 8$ Hz, CH ₂ -Hg), 1.4-1.9 (multiplet, 6 H, CH ₂), 1.2-1.3 (doublet, 3 H, $J = 5$ Hz, CH ₃)	(KBr) 2950 and 2920 (CH), 1710 (C=O), 1450, 1270 (C-O), 1170, 1120, 710	Calcd for C ₁₈ H ₂₂ NO ₂ HgCl: C, 38.78; H, 4.44; N, 2.82; Hg, 40.40; Cl, 7.07. Found: C, 38.55; H, 4.47; N, 2.76; Hg, 40.10; Cl, 6.82.

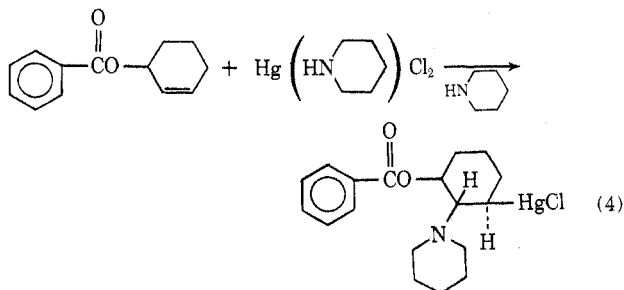
^a Amines which gave no addition products under these conditions were pyrrolidine, 4-methylpiperazine, 3-methylpiperidine, heptamethyleneimine, and diethylamine.

allyl benzoates (-OH, -OCH₃) formed addition products whereas allyl *p*-nitrobenzoate failed to react.

No additions were observed in the allylcarbinyl benzoate system (eight-membered ring), the 4-pentenyl acetate system (nine-membered ring), or in the methyl vinyl acetate system (six-membered ring). Compounds with very rigid structures, such as the bicyclo-[2.2.1]-5-heptenes, failed to yield addition products even though they would conform to a seven-membered ring intermediate (eq 3).



The stereochemistry of the addition can be observed in the case of the product **6** from 3-cyclohexen-1-yl benzoate. The large coupling constant for axial protons ($J = 10$ cps) in the nmr indicates that the -NR₂ and -HgCl groups are trans to each other (eq 4). This



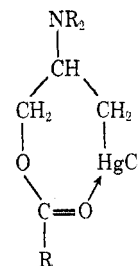
is in agreement with what is observed in oxymercuration (trans addition) in the cases of nonsterically hindered olefins.¹⁻³

The infrared carbonyl absorption frequencies of the aminomercuration products were shifted to lower frequencies (Table III). This indicates a weakening of

TABLE III

Compd	Normal, cm ⁻¹	Aminomercuration product, cm ⁻¹	$\Delta C=O$, cm ⁻¹
Aryl esters	1750-1735	1710-1680	~50
Urea	~1660	1600	~60
Urethane	1740-1690	1650	~40

the carbonyl bond, perhaps by coordination to the chloromercuri substituent.



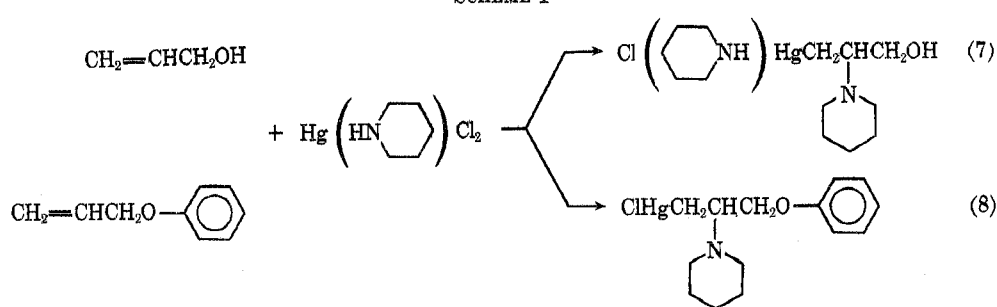
This would be one explanation for the observed magnetic nonequivalence of the two hydrogens adjacent to oxygen.¹⁰ Alternatively, this nonequivalence could be ascribed to the presence of the adjacent asymmetric carbon carrying the amino group.

(10) We are indebted to Dr. G. Noren for pointing this out.

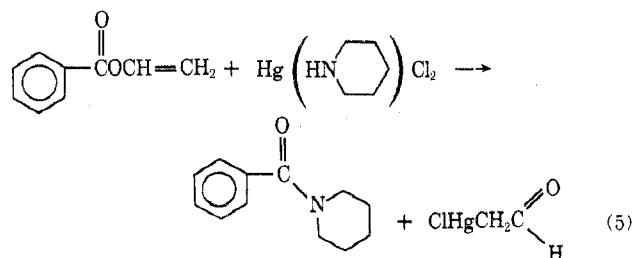
TABLE IV
 AMINOMERCURATION ADDUCTS FROM OLEFINIC ALCOHOLS AND ETHERS WITH PIPERIDINE

Olefin	Chemical Structure	No.	Yield, %	Mp, °C	Recrystn solvent	Nmr, δ	Ir, cm^{-1}	Anal.
Allyl alcohol	$\text{HOCH}_2\text{CH}(\text{N})\text{CH}_2\text{Hg}(\text{HN})\text{Cl}$	13	74	67-68		(CDCl_3) 4.5 (singlet, 2H, NH, OH), 3.4-3.6 (doublet, 2H, $J = 8$ Hz, CH_2O), 2.9-3.3 (multiplet, 4H, CH_2NHg), 2.5-2.7 (multiplet, 4H, CH_2N), 1.9-2.1 (doublet, 2H, $J = 8$ Hz, CH_2Hg), 1.4-1.9 (multiplet, 12H, CH_2)	(KBr) 3300 (NH, OH), 2920 (CH), 1410, 1110, 1095, 1025 (CO), 860, 760, 735	Calcd for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{Hg}$ OHgCl: C, 33.76; H, 5.84; N, 6.06; Hg, 43.29; Cl, 7.57. Found: C, 33.76; H, 5.92; N, 6.07; Hg, 42.90; Cl, 7.44.
3-Buten-1-ol	$\text{HOCH}_2\text{CH}_2\text{CH}(\text{N})\text{CH}_2\text{Hg}(\text{HN})\text{Cl}$	14	53	68		(CDCl_3) 5.3 (singlet, 2H, NH and OH), 3.6-3.9 (multiplet, 2H, CH_2O), 2.9-3.2 (multiplet, 5H, CH_2NH and CHN), 2.5-2.8 (multiplet, 4H, CH_2N), 1.9-2.1 (doublet, 2H, $J = 8$ Hz, CH_2Hg), 1.4-1.8 (multiplet, 14H, CH_2)	(KBr) 3160 (OH), 2900 (CH), 1445, 1110, 1090, 1040, 950, 880, 870	Calcd for $\text{C}_{14}\text{H}_{23}\text{N}_2\text{Hg}$ OHgCl: C, 35.29; H, 6.09; N, 5.88; Hg, 42.01; Cl, 7.35. Found: C, 35.04, H, 6.16; N, 5.62; Hg, 41.77; Cl, 7.30.
4-Penten-1-ol	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{N})\text{CH}_2\text{Hg}(\text{HN})\text{Cl}$	15	88	Oil		(CDCl_3) 5.1 (singlet, 2H, NH and OH), 3.6-3.7 (multiplet, 2H, CH_2O), 3.0-3.3 (multiplet, 5H, CH_2NHg and CHN), 2.6-2.8 (multiplet, 4H, CH_2N), 2.1-2.3 (doublet, 2H, $J = 8$ Hz, CH_2Hg), 1.5-1.9 (multiplet, 16H, CH_2)	(neat) 3400-3200 (OH, NH), 2950 (CH), 1650 (CN), 1480, 1100, 1050 (CO), 870, 810, 750	
Diallyl ether	$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}(\text{N})\text{CH}_2\text{Hg}(\text{HN})\text{Cl}$	16	40	Oil		(CDCl_3) 5.6-5.9 (multiplet, 1H, $\text{CH}=\text{}$), 5.4 (singlet, 1H, NH), 5.0-5.3 (doublet, 2H, $J = 12$ Hz, $\text{CH}_2=\text{}$), 3.8-4.0 (doublet, 2H, $J = 6$ Hz, CH_2O), 3.3-3.7 (octet, 2H, $J = 4$ Hz, CH_2O), 2.7-3.1 (multiplet, 4H, CH_2NH), 2.3-2.7 (multiplet, 4H, CH_2N), 1.9-2.1 (doublet, 2H, $J = 8$ Hz, CH_2Hg), 1.3-1.8 (multiplet, 12H, CH_2)	(neat) 3030 ($\text{CH}=\text{}$), 2910 (CH), 1645 (C=C), 1450, 1110, 1000, 930, 870, 760	
Allyl phenyl ether	$\text{CH}_2=\text{CHCH}_2\text{OCH}(\text{N})\text{CH}_2\text{Hg}(\text{HN})\text{Cl}$	17	46	75	Absolute ethanol	(CDCl_3) 6.8-7.4 (multiplet, 5H, phenyl), 3.7-4.3 (octet, 2H, $J = 4$ Hz, CH_2O), 2.9-3.3 (multiplet, 1H, CHN), 2.5-2.7 (multiplet, 4H, CH_2N), 2.1-2.2 (doublet, 2H, $J = 8$ Hz, CH_2Hg), 1.4-1.7 (multiplet, 6H, CH_2)	(KBr) 3050, 2910 (CH), 1580, 1490, 1460, 1240 (CO), 1170, 1100, 1040, 885, 755, 690	Calcd for $\text{C}_{14}\text{H}_{20}\text{NO}$ HgCl: C, 37.08; H, 4.41; N, 3.09; Hg, 44.15; Cl, 7.72. Found: C, 36.89; H, 4.48; N, 2.90; Hg, 43.85; Cl, 7.36.

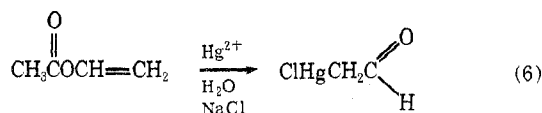
SCHEME I



Vinyl Esters.—Vinyl benzoate and vinyl acetate undergo an aminolysis-oxidation reaction under the aminomercuration conditions to produce *N*-benzoyl-piperidine and chloromercuriacetaldehyde (eq 5).



This is in agreement with the work of Nesmeyanov, *et al.*,¹¹ who found that vinyl acetate yielded chloromercuriacetaldehyde under oxymercuration conditions (eq 6). It is not necessary, however, for carbonyl co-

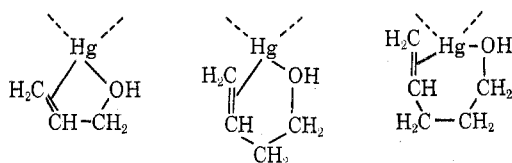


ordination to occur in these examples since vinyl ethers also produce chloromercuriacetaldehyde.¹¹

Allylic Alcohols and Ethers.—We also found that unsaturated alcohols and ethers will undergo the aminomercuration reaction (Scheme I). The olefinic compounds listed in Table IV were found to yield addition products. In some cases, the addition product could only be obtained crystalline from the piperidine solvent and a molecule of the amine was found in the mercuric ion coordination sphere (eq 7).

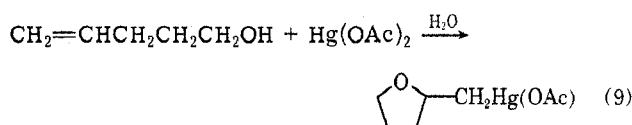
(It is interesting to note that the addition product obtained from allyl alcohol was identical with that obtained from allyl acetate. This indicates that aminolysis is a competing reaction in the case of allyl esters.)

The saturated alcohol systems appear to be much more flexible than the carbonyl-containing olefins in that the geometry requirements are less stringent. Allyl alcohol, 3-buten-1-ol, and 4-penten-1-ol, which could form intermediates consisting of five-, six-, and seven-membered rings, were all found to give addition products.

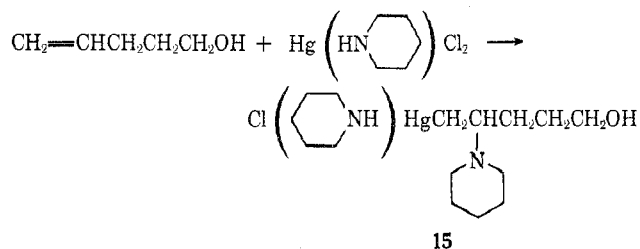


(11) A. Nesmeyanov, I. Lutsenko, and R. Tumanova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 601 (1949).

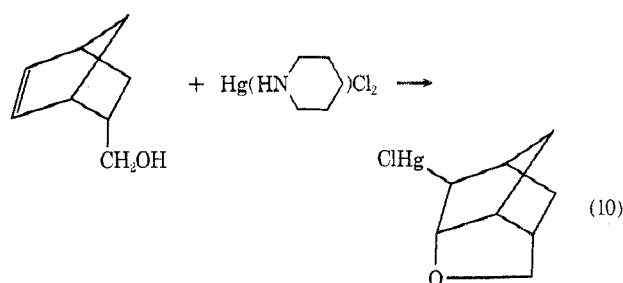
In the oxymercuration of 4-penten-1-ol, the hydroxyl group in the substrate is able to participate in the reaction and a tetrahydrofuran derivative is formed¹² (eq 9). This reaction does not compete under amino-



mercuration conditions since only an aminomercurial product is observed.



Bicyclo[2.2.1]-5-hepten-2-methanol,¹¹ however, undergoes internal oxymercuration even in the presence of an amine solvent to produce the known tricyclic ether (eq 10).



Conclusion

Aminomercuration is not so general a reaction as oxymercuration. However, aminomercuration reactions can be carried out with olefins which possess internal coordinating groups. The effects of structural changes in both the olefin and the amine have been explored.

Experimental Section

All melting points are uncorrected. Nuclear magnetic resonance spectra were taken on Varian HA-100 and T-60 spec-

(12) M. Lora-Tamayo, F. Martín-Panizo, and F. Bonnet, *An. Real Soc. Espan. Fis. Quím., Ser. B*, **51**, 711 (1955); *Chem. Abstr.*, **50**, 11246 (1956).

TABLE V
 ADDUCTS OF AMINES WITH MERCURIC CHLORIDE

Registry no.	1:1 Complex HgCl ₂ -Amine	Mp, °C	Calcd					Anal, %					
			C	H	N	Hg	Cl	C	H	N	Hg	Cl	
34805-71-5	Piperidine	142	16.85	3.09	3.93	56.52	20.00				3.77	55.92	19.74
34805-72-6	4-Pipecoline	159	19.64	3.51	3.78	54.05	19.19	19.42	3.53	3.74	54.24	18.87	
34805-73-7	3-Pipecoline	149	19.64	3.51	3.78	54.05	19.19	19.75	3.56	3.88	54.27	18.95	
34805-74-8	2-Pipecoline	106	19.64	3.51	3.78	54.05	19.19	19.07	3.44	3.76	54.41	18.92	
34805-75-9	Hexamethyleneimine	141											
34805-76-0	Ethylamine	179	7.94	2.21	4.43	63.29	22.46	7.70	2.12	4.62	64.30	20.56	
34805-77-1	Morpholine	151	13.40	2.51	3.91	55.86	19.83	13.26	2.44	3.93	55.93	19.57	

trometers. Infrared spectra were taken on Perkin-Elmer 337 and Infracord spectrometers. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

A typical preparation of an amine-mercuric chloride complex was as follows.

Mercuric Chloride-Piperidine Complex.—To a solution of 8.1 g (0.08 mol) of mercuric chloride in 120 ml of hot water was added a solution of 2.5 g (0.03 mol) of piperidine (Aldrich) in 10 ml of water while stirring vigorously with a magnetic stir bar. A yellow precipitate separated out of solution immediately. The precipitate was filtered, washed with water, and air dried overnight. The light yellow solid (10.2 g, 100%) melted at 142–143°.

Other 1:1 mercuric chloride-amine complexes were formed in an analogous manner and are summarized in Table V. A typical aminomercuration reaction was as follows.

3-Chloromercuric-2-piperidinopropyl Benzoate (1).—To a solution of 5.0 g (0.030 mol) of allyl benzoate (K & K Laboratories) in 35 ml of piperidine (Aldrich) was added 6.0 g (0.016 mol) of mercuric chloride-piperidine complex. The suspension was stirred with a magnetic stir bar. After 1 hr, the solution was homogeneous, and after 36 hr, piperidine hydrochloride began to precipitate from the solution. Stirring was continued for another 36 hr. The solution was filtered and the excess piperidine was removed with the aid of a vacuum pump. The resulting yellow oil was dissolved in absolute ethanol and allowed to crystallize. The product was filtered, yielding 5.0 g (65%), mp 115–116°.

Esters.—Methyl allylacetate, bp 120–122° (lit.¹² bp 125–126°), was prepared by reaction of allyl acetyl chloride with methanol. 2-Cyclohexen-1-ol benzoate was prepared from 2-cyclohexen-1-ol (Aldrich) and benzoyl chloride in pyridine, bp 97° (0.2 mm) [lit.¹³ bp 160–165° (15 mm)]. *endo*-Bicyclo[2.2.1]hepten-2-yl benzoate was prepared from the reaction of cyclopentadiene with vinyl benzoate for 20 hr at 200° (autoclave), bp 98° (0.2 mm).

Anal. Calcd for C₁₄H₁₄O₂: C, 78.50; H, 6.54; O, 14.95. Found: C, 78.62; H, 6.69; O, 15.66.

4-Chloromercuri-6-oxatricyclo[3.2.1.2^{3,8}]nonane.—To a solution of 3.0 g (0.024 mol) of *endo*-bicyclo[2.2.1]-5-hepten-2-methanol (K & K Laboratories) in 40 ml of piperidine was added 6.0 g (0.016 mol) of mercuric chloride-piperidine complex. The solution was stirred with the aid of a magnetic stir bar for 4 days. Piperidine hydrochloride was filtered from the reaction mixture and the filtrate was evaporated to an oil with the aid of a vacuum pump. The resulting oil was dissolved in absolute alcohol, and ether was added until cloudy. After standing overnight, the crystals were filtered, yielding 4.2 g (60%) of product: mp 205° (lit.¹⁴ mp 227° from benzene-petroleum ether); nmr spectrum (DMSO-*d*₆) 4.6–4.7 (doublet, 1 H, *J* = 4 Hz, CHO), 3.4–3.6 (multiplet, 2 H, CH₂O), 3.2–3.3 (multiplet, 1 H, CH bridgehead), 3.0–3.1 (multiplet, 1 H, CH bridgehead), 2.2–2.4 (multiplet, 2 H, 9-CH and 1-CH), 2.0–2.1 (multiplet, 1 H, CHHg), 1.4–1.7 (quartet, 2 H, *J* = 12 Hz, 2-CH₂), 0.9–1.1 ppm (doublet, 1 H, *J* = 12 Hz, 9-CH); ir spectrum (KBr) 2950, 2900, 2850 (CH), 1295, 1240, 1140, 1050, 1030, 1015, 950, 900 cm⁻¹.

Anal. Calcd for C₉H₁₁O₂HgCl: C, 26.88; H, 3.07; Hg, 55.86; Cl, 9.93. Found: C, 26.80; H, 3.45; Hg, 55.05; Cl, 10.10.

Registry No.—1, 34792-29-5; 2, 34792-30-8; 3, 34805-78-2; 4, 34805-79-3; 5, 34805-80-6; 6, 34805-81-7; 7, 34805-82-8; 8, 34805-83-9; 9, 34805-84-0; 10, 34805-85-1; 11, 34805-86-2; 12, 34805-87-3; 14, 34805-88-4; 15, 34805-89-5; 16, 34805-90-8; 17, 34805-91-9; *endo*-bicyclo[2.2.1]hepten-2-yl benzoate, 34805-92-0; 4-chloromercuri-6-oxatricyclo[3.2.1.2^{3,8}]nonane, 34805-93-1.

Acknowledgment.—We wish to thank the National Science Foundation and the Hercules Company for the support of this work.

(14) H. Henbest and B. Nicholls, *J. Chem. Soc.*, 227 (1959). We have no explanation for this discrepancy in melting points.

(13) Koetz and Richter, *J. Prakt. Chem.*, [2] 111, 385.