Reactions of Amines and Mercury(II) Salts with Alkenes at Elevated Pressures

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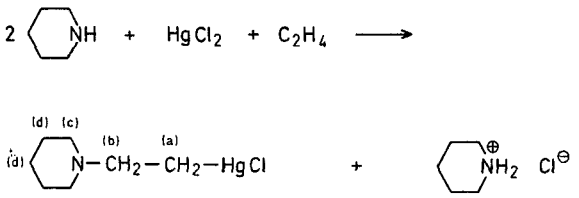
Although the additions of mercury (II) salts and alcohols to alkenes to give β-alkoxymercurials proceed readily in very high yields[1], the published accounts of the analogous aminomercuration reactions indicate that they proceed only sluggishly to give low yields of isolable products; and frequently the products are unstable oils. In contrast, we have found that reactions carried out at elevated pressures, where applicable, occur rapidly and may lead to the formation of crystallizable solids not obtained at ordinary pressures. Some examples are reported here.

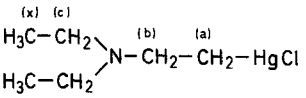
The first aminomercuration reaction, reported by Freidlina and Kochetkova[2], and later repeated by Périé and Lattes[3] who followed the reaction progress with time, required 16 to 50 hours to reach completion.



1

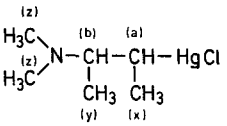
Using initial ethylene pressures of 600 psi in a simple 45 ml bomb equipped with pressure gauge, we have obtained in only one to two hours yields of *N*-(2-chloromercuriethyl)-piperidine (**1**) equal to or greater than those achieved in the low pressure runs. Average yields are 80%, based on the amount of piperidine hydrochloride recovered.

The reaction of ethylene with diethylamine and mercuric chloride has been reported to yield an unstable yellow oil[4]. Using ethylene at an initial pressure of 600 psi, *N*-(2-chloromercuriethyl)diethylamine (**2**) is obtained as a tan solid in 38% yield. Multiple recrystallizations yield a white material of reasonable stability.



2

Syntheses attempted in this laboratory using various amines and the 2-butenes at atmospheric pressure led to the formation of oils from *cis*-2-butene and no product from *trans*-2-butene. By combining liquified dimethylamine and 2-butene with mercuric chloride, and carrying out the reaction under the pressure developed as the liquids vaporized at room temperature in a 45 ml bomb, a solid product (**3**), *N,N*-1-trimethyl-2-chloromercuripropylamine is regularly obtained from *cis*-2-butene, and a solid is obtained in poor yield in about 10% of the attempts using *trans*-2-butene.



3

Additional reactions of various secondary aliphatic amines (dimethylamine, di-*n*-butylamine, pipecolines) and gaseous alkenes (propylene and isobutene) at elevated pressures afforded in every case shorter reaction times and higher yields than those obtained in low pressure experiments.

***N*-(2-Chloromercuriethyl)piperidine (1):**

To piperidine (20 ml) in a 45 ml bomb (Parr, Model 4712, with Model 4316 gauge block, in T303 stainless steel) mercury (II) chloride (3.0 g) was added slowly with stirring. After closing the bomb and rapidly evacuating most of the air, 600 psi of

ethylene was admitted. With stirring a rapid pressure drop occurred and the system was repressurized once to 600 psi. After 10—15 minutes of continued absorption the pressure stabilized at about 350 psi. After 1 hour the system was slowly depressurized. Filtration gave piperidine hydrochloride (1.1 g, 85% yield), identified by I.R. and m.p. Excess piperidine was removed under vacuum at room temperature, and the product was dissolved in a 2:1 mixture of anhydrous ethanol and ether. Filtering removed the insoluble complex, piperidinemercury(II) chloride, $C_5H_{10}NH \cdot HgCl_2$; m.p. 167°; sharp N—H stretch, 3120 cm^{-1}.

Multiple recrystallizations of crude **1** yielded 0.96 g (25%); m.p. 77.5—78.5° (lit.[3] 77.5—78.0°) (from mixed solvent or pure ether). When an entire reaction mixture was reduced with basic sodium borohydride, the yield of *N*-ethylpiperidine (by G.L.C.) was comparable to that of the piperidine hydrochloride, indicating that the low yield of pure **1** is due to its decomposition (indicated by precipitation of elemental mercury) during the recrystallizations. Once the material is obtained in pure form it is stable for several weeks.

I.R. (KBr): ν_{max} = 2940, 2920, 2800, 2760, 1455, 1315, 1150, 1110, 1095, 980, 785, 695 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 2.20 (m, H(a), J = 7.2 Hz), 2.59 (m, H(b)), 2.42 (m, H(c)), 1.52 ppm (m, H(d)), $J_{^{199}Hg-H(a)}$ = 206 Hz, $J_{^{199}Hg-H(b)}$ = 256 Hz.

Mass spectrum: *m/e* (based on ^{202}Hg and ^{35}Cl) = 349(M^+), 320, 265, 237, 202, 112, 98. (*m/e* = 98, presumably $[(CH_2)_5N{=}CH_2]^{\oplus}$, is the most intense peak.)

***N*-(2-Chloromercuriethyl)diethylamine (2)**:
Synthesis and purification procedures were the same as those for **1** except that the final recrystallizations were done alternately from anhydrous ethanol and ether, giving white solid **2** in an average yield of 25%, m.p. 47—48°.

$C_6H_{14}NHgCl$	calc.	C 21.43	H 4.20	N 4.16	Hg 59.66	Cl 10.54
(336.23)	found	21.43	4.22	4.19	59.75	10.49

I.R. (nujol): ν_{max} = 2850, 1440, 1200, 1130, 1070, 1000, 765, 685, 640 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 2.22 (m, H(a), J = 7.2 Hz), 2.72 (m, H(b)), 2.58 (q, H(c), J = 7.0 Hz), 1.03 ppm (t, H(x)), $J_{^{199}Hg-H(a)}$ = 202 Hz, $J_{^{199}Hg-H(b)}$ = 253 Hz.

Mass spectrum: *m/e* (based on ^{202}Hg and ^{35}Cl) = 337 (M^+), 322, 294, 265, 237, 202, 86 (the latter, presumably $(C_2H_5)_2N^+{=}CH_2$, is the most intense peak).

***N,N*,1-Trimethyl-2-chloromercuripropylamine (3)**:
To liquified dimethylamine (20 ml) in a 45 ml bomb was added mercuric chloride (4.0 g) with stirring, followed by liquified *cis*-2-butene (6 ml). The bomb was capped, warmed briefly to 40° and shaken at room temperature for 6 hr. After cooling in dry ice, the bomb was opened, the solution quickly filtered and concentrated to a white solid under vacuum. Filtration of an anhydrous ether solution of the solid removed insoluble amine-mercuric chloride complex, and recrystallization gave **3**; yield: 1.2 g (24%); m.p. 101—102°.

$C_6H_{14}NHgCl$	calc.	C 21.43	H 4.20	N 4.16	Hg 59.66	Cl 10.54
(336.23)	found	21.55	4.17	4.13	59.95	10.46

I.R. (KBr): ν_{max} = 2980, 2940, 2870, 2830, 2790, 1450, 1150, 1090, 1080, 1030, 995, 935, 855, 770 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 2.7 (m, H(a), H(b)), 0.90 (d, H(y), J = 6.2 Hz), 1.41(d, H(x), J = 7.0 Hz), 2.22 ppm (s, H(z)), $J_{^{199}Hg-H(x)}$ = 302 Hz, $J_{^{199}Hg-H(y)}$ = 24 Hz.

Mass spectrum: *m/e* (based on ^{202}Hg and ^{35}Cl) = 337(M^+), 322, 280, 237, 202, 100, 72. (*m/e* = 72, presumably $(CH_3)_2N^+{=}CHCH_3$, is the most intense peak.)

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