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CATALYTIC AMINOMERCURATION OF OLEFINS IN A TANDEM AMINOMERCURATION-DEOXYMERCURATION; ONE-STEP SYNTHESIS OF SECONDARY N-ARYLALLYLAMINES FROM ALLYLALCOHOLS

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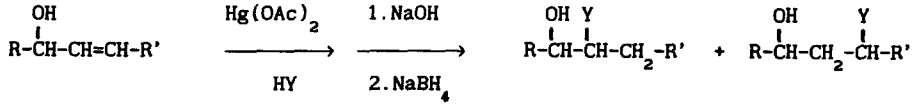
Abstract - Allyl alcohols react with primary aromatic amines and stoichiometric amounts of mercury(II) tetrafluoroborate to give mixtures of mono- and diallyl anilines. However, the use of the tandem aminomercuration-deoxymercuration promoted by catalytic mercury(II) tetrafluoroborate allows to perform regiospecifically the monoallylation reaction with very high yields. A mechanism is proposed to account for the observed results.

INTRODUCTION

The solvomercuration of alkenes with mercury (II) acetate is a widely used synthetic methodology for the Markownikoff addition of nucleophiles to the C=C double bound. This reaction, when performed on alkenes supporting a preexisting function allows the preparation of difunctional compounds and also of saturated heterocycles.[1,2] In this context, the solvomercuration of allylic alcohols provides a suitable route to 1,2- and 1,3-diols and aminoalcohols.[1,2] The regioisomers distribution depends on the substitution pattern in the starting allyl alcohol (Scheme 1).

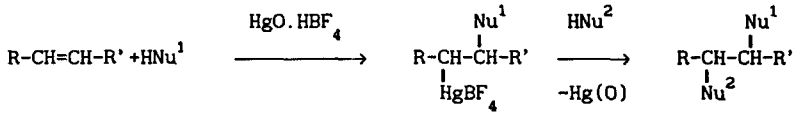


R, R' = H, Alkyl
Y = O, NHAr

Scheme 1

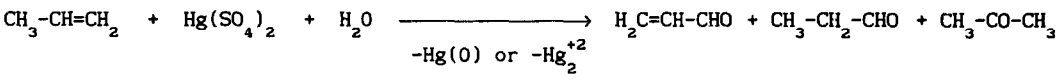
Nevertheless none report concerning to the solvomercuration of these substrates with

other mercury(II) salts has appeared in spite of the different course of the solvomercuration when carried out with mercury (II) salts derived from strong mineral acids such as tetrafluoroboric.[3,4] So, the reaction of stoichiometric amounts of mercury (II) acetate with simple olefins or dienes give stable oxy- or aminomercurials, while the same reaction using mercury (II) tetrafluoroborate occurs with spontaneous reduction of mercury which is displaced by a second molecule of nucleophile in an oxidative demercuration process, (Scheme 2).



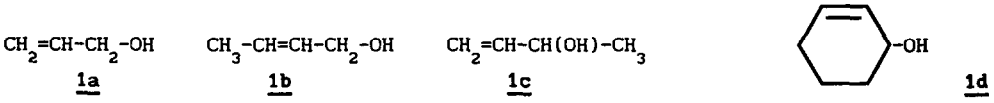
Scheme 2

It is also well established that the oxidation of olefins with aqueous mercuric sulfate or nitrate in the so-called Deniges reaction[5] occurs with formation of α,β-unsaturated carbonyl compounds and saturated oxidation products in a reaction which proceeds through an intermediate allyl alcohol with reduction of mercury[6] (Scheme 3)



Scheme 3

All the above facts prompt us to explore the aminomercuration of allylic alcohols **1** with mercury (II) tetrafluoroborate to determine the influence, if any, of the preexisting

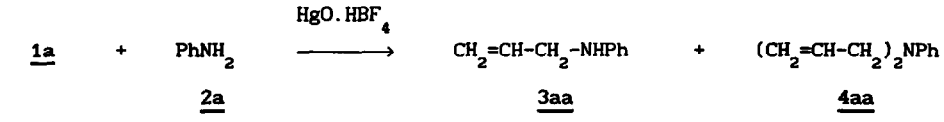


alcohol function on the demercuration step. Unexpectedly, we have found that allylic alcohols act under these conditions as simple allylating agents towards the amine while mercury (II) does not undergo any reduction but behaves as a catalyst. In this way, we have developed a convenient one step route to N-aryl substituted secondary allylamines. These compounds were not accessible previously by direct allylation and their preparation required the use of a tedious purification procedure *via* the N-nitrosoamine,[7] due to polyallylation.

Several methodologies have been used for primary allylamines and secondary N-alkylallylamines including the use of imidates and imines as precursors.[8]

RESULTS AND DISCUSSION

The aminomercuration of allyl alcohol **1a** using different molar ratios of amine/mercury(II) tetrafluoroborate, in THF as the solvent, gives N-allylamines **3aa** and **4aa**, (Scheme 4).



Scheme 4

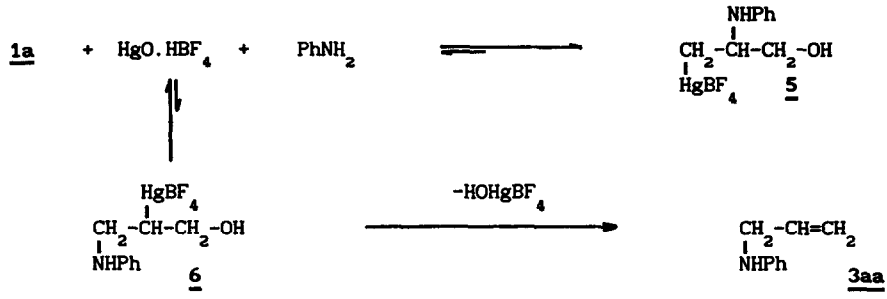
Different reaction conditions have been tested as summarized in Table I. The amount of mercury(II) salt employed affects dramatically the ratio of mono- *versus* diallylation (see runs 1 and 2 or 3 and 4) obtained. Only monoallylation products are obtained when the mercury(II) salt is used just as a catalyst. The reaction rate increases with the temperature (runs 2 and 4) and it is interesting to remark that oxidative demercuration was not observed to occur in any extent even at 80°C. From the above results it appears that the first step in the allylation reaction should be the Markownikoff aminomercuration of the olefin. However, it has been shown [1] that in the oxymercuration of allylic alcohols with

Table I. Aminomercuration of 2-propenol **1a** with aniline **2a**

Run	Hg(II)/**2a**/**1a** molar ratio	Temperature °C	Reaction Time h	Products Yield(%)[a] **3aa**	**4aa**
1	1/2/3	25	72	70	80
2	1/10/15	25	72	230	-
3	1/2/3	80	6	68	180
4	1/10/15	80	10	396	-
5	1/20/30	80	24	678	-
6	1/100/150	80	24	2940	-

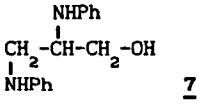
[a] *Based on mercury(II) salt.*

mercury(II) acetate the Markownikoff oriented adduct is in equilibrium with a minor amount of the corresponding anti-Markownikoff oriented isomer. We shown that also the aminomercuration of olefins is a reversible process when the mercury (II) salt derives from a strong acid.[9] So, in the presence of tetrafluoroboric acid, the anti-Markownikoff aminomercurial 6 undergoes an acid-promoted deoxymercuration with displacement of the



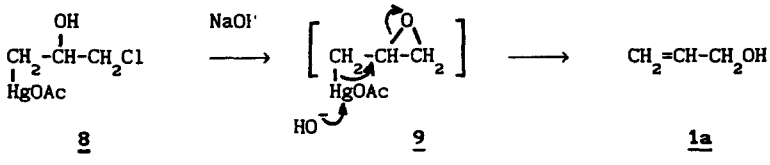
Scheme 5

equilibrium towards the formation of the allylamine 3aa (Scheme 5). The formation of the diamination product 7 was not even detected showing that the deoxymercuration of 6 is faster than the oxidative reduction by the amine.



On the other hand, to check the possibility that allylaniline 3aa could undergo interchange of amine with the excess of aniline in the reaction medium we attempted the reaction of o-bromoaniline and catalytic mercury(II) tetrafluoroborate with allylaniline, but all reagents were recovered unchanged showing that allylaniline is not an efficient allylation agent.

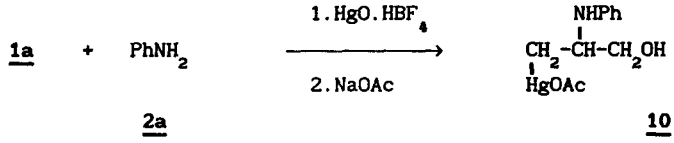
Moreover, Brown has found that the oxymercurial 8, obtained in the reaction of allyl chloride and mercury(II) acetate, is rapidly converted into allyl alcohol by the action of



Scheme 6

bases[2] (Scheme 6). In order to rule out a similar mechanism for the formation of allylaniline in the work-up of the reaction, the aminomercuration of **1a** was set aside for 6 hours at 80°C and the solvent evaporated. The ^{1}H-NMR analysis of the crude reaction mixture indicates that the allylamine was already formed in the usual high yield in absence of bases.

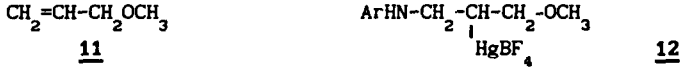
On the other hand, the off-resonance analysis of the adduct **10** obtained by aminomercuration of allyl alcohol (room temperature, 30 min stirring followed by anionic



Scheme 7

exchange with sodium acetate) showed the same structure for this adduct and the one obtained when mercury (II) acetate is used as the mercurating agent (Scheme 7).

On the other hand, allylmethylether **11** failed to give the allylamine in good yields. This



suggests that the attack of mercury to the internal carbon to give the intermediate **12** occurs with more difficulty probably due to steric crowding.

Table II. Aminomercuration of allylic alcohols **1** with aromatic amines **2**

Alcohol	Amine X in $(X)C_6H_4NH_2$		Product[a]	Molecular Formula	(M.W.)	Yield(%)[b]	Yield(%)[c]
1a	H	**2a**	**3aa**			396	39.6
1a	p-CH_3	**2b**	**3ab**	$C_{10}H_{13}N$	(147)	267	26.7
1a	o-Br	**2c**	**3ac**	$C_9H_{10}BrN$	(212)	487	48.7
1b	o-Br	**2c**	**3bc**	$C_{10}H_{12}BrN$	(226)	250	25.0
1c	H	**2a**	**3ca**(Z+E)			422	42.2
1c	p-CH_3	**2b**	**3cb**(Z+E)	$C_{11}H_{15}N$	(173)	218	21.8
1c	o-Br	**2c**	**3cc**(Z+E)	$C_{10}H_{12}BrN$	(226)	583	58.3
1d	H	**2a**	**3da**			820	82.0
1d	o-Br	**2c**	**3dc**	$C_{12}H_{14}BrN$	(252)	648	64.8

[a] *All new compounds gave satisfactory microanalysis within ± 0.3 of the theoretic values.* [b] *Based on mercury(II) salt.* [c] *Based on amine.*

We have studied the generalization of this reaction to representative allylic alcohol and aromatic amines. The aminomercuration of 2-butenol **1b** gives the allylamine **3b** . In contrast 3-buten-2-ol **1c** is transformed in a nearly equimolecular mixture of the Z/E isomers of 2-butenylamine **3c**. When 2-cyclohexenol **1d** is used the monoallylamine **2d** is obtained with very high yields. However, 2-methyl-2-propenol failed to give the corresponding allylamine showing that the equilibrium between the external **5** and the internal aminomercurial **6** lies towards the Markownikoff adduct due to the electronic directing effect of the methyl group. It has been shown[10] that anti-Markownikoff addition is not observed in the solvomercuration of disubstituted terminal olefins $R_2C=CH_2$ in any extent.

Other aromatic primary amines with representative substitution patterns were also essayed Best yields are obtained with less basic aromatic amines such as o-bromoaniline. As the basicity of the aromatic amine increases the degree of transformation decreases. This could be correlated to the enhanced ability of the lone pair of the amine to coordinate with the mercury.

CONCLUSIONS

Although the oxymercuration and aminomercuration of olefins has been subject of continue interest over this century this is to our knowledgement the first report in which the tandem aminomercuration-deoxymercuration is described providing a new synthetic strategy in which mercury(II) salts are involved as catalysts in reactions with alkenes. On the other hand, it should be pointed out that unlike allylic aliphatic amines, for which many synthetic methods are available, allylic aromatic amines have been synthesized only by a limited number of procedures. The most general method[11] uses allyl halides as substrates but mixtures of N-allylamines and N,N-diallylamines are obtained from primary amines. However, the allylation of aromatic amines by allyl alcohols in the presence of catalytic mercury(II) tetrafluoroborate, provides a new, simple and convenient one step procedure for the regiospecific monoallylation of primary aromatic amines with excellent yields.

EXPERIMENTAL

^1H and ^{13}C N.m.r. spectra were recorded in a Bruker WP-80 (80 MHz)n.m.r. spectrometer. I.r. spectra were recorded in a Perkin Elmer Model 843 i.r. spectrometer. Mass spectra were measured on a Hewlett Packard Model 5930A mass spectrometer. Allylic alcohols and aromatic amines were commercially available and were used as received. Mercury(II) tetrafluoroborate was prepared as previously reported.[3a]

Typical Experimental Procedure for Compounds **3** *(Table II)*

Mixtures of allylic alcohol (15 mmol), mercury(II) tetrafluoroborate (1 mmol) and aromatic amine (10 mmol) in THF (40 mL) were stirred for ten hours at 80°C. Afterwards, the reaction

mixture was treated with 3N KOH and the solution was extracted with ether. The organic layer was evaporated to give an oily residue which was purified by preparative column chromatography (silica gel, hexane-ethyl acetate 10:1).

N-(2-propenyl)aniline(3aa):For IR, ^{1}H-NMR and MS see literature[12]; $\delta_C(CDCl_3)$ 147.78(s), 135.31(d), 128.76(d), 117.02(d), 115.44(t), 112.67(d), 45.98(t).

N-(2-propenyl)-p-toluidine (3ab): $\nu_{max}(CCl_4)$ 3440, 3020, 1550, 1320, 1260, 1240, 1000, 940; $\delta_H(CDCl_3)$ 6.1-6.7(4H, m), 5.3-6.0(1H, m), 4.7-5.3(2H, m),3.35(2H, m), 3.2(1H, s), 2.0(3H, s);$\delta_C(CDCl_3)$ 145.67(s) 135.66(d) 129.50(d) ,126.41(s), 115.69(t), 113.10(d), 46.70(t), 20.14(q); m/z: 147(M^+), 132, 120, 41.

N-(2-propenyl)-o-bromoaniline(3ac): $\nu_{max}(CCl_4)$ 3420, 3060, 1700, 1600, 1400, 1120, 1020; $\delta_H(CDCl_3)$ 6.1-7.2(4H, m), 5.4-6.0(1H, m), 4.8-5.2(2H, m), 4.2(1H, bb), 3.5(2H, m); $\delta_C(CDCl_3)$ 144.52(s), 134.50(d),132.07(d), 128.16(d), 117.59(d), 115.92(d), 111.39(d), 109.51(s), 45.87(t); m/z: 213, 211(M^+), 132, 41.

N-(2-but-3-enyl)-o-bromoaniline (3bc):$\nu_{max}(CCl_4)$ 3410, 3000, 1550, 1320, 1260, 1220, 1020, 920; $\delta_H(CDCl_3)$ 6.1-7.2(4H, m), 5.3-5.9(1H, m), 4.7-5(2H, m),4.95(1H, m), 3,7(1H, s), 1.15(3H, d); $\delta_C(CDCl_3)$ 143.97(s), 140.40(d), 132.10(d), 128.07(d), 117.47(d), 113.98(t), 112.29(d), 109.60(s), 50.86(t), 21.37(q); m/z: 227, 225(M^+), 212, 210, 200, 198, 145, 55.

N-(2-butenyl)aniline (3ca) $\nu_{max}(CCl_4)$ 3420, 2960, 1600, 1500, 1320, 1260, 960; $\delta_C(CDCl_3)$ 148.90(s), 148.85(s), 129.65(d), 128.88(d), 128.58(d), 127.95(d), 127.21(d), 117.88(d), 117.78(d), 113.50(d), 46.43(d), 41.39(d), 18.13(q),13.50(q). For ^{1}H-NMR see literature.[13]

N-(2-butenyl)-p-toluidine (3cb): $\nu_{max}(CCl_4)$ 3400, 2960, 1550, 1240, 1220, 1010, 980; $\delta_H(DCCl_3)$ 6.2-6.9(4H, m), 5.3-5.6(2H, m), 3.4-3.6(2H, m), 3.2(1H, s), 2.1(3H, s), 1.55(3H, d); $\delta_C(DCCl_3)$ 145.63(s), 129.09(d), 128.08(d), 127.83(d), 126.58(d), 125.75(s), 125.60(s), 112.48(d), 45.62(t), 40.61(t), 19.73(q), 19.73(q), 17.00(q); m/z: 161(M^+), 146, 120, 55.

N-(2-butenyl)-o-bromoaniline (3cc): $\nu_{max}(CCl_4)$ 3420, 2960, 1550, 1320, 1240, 1020, 980;.$\delta_H(DCCl_3)$ 6.0-7.0(4H, m), 5.1-5.2(2H, m), 3.9(1H, s), 3.3(2H, m), 1.35(3H, d); $\delta_C(DCCl_3)$ 144.33(s), 144.25(s), 131.61(d), 127.72(d), 127.13(d), 126.82(d), 126.61(d), 117.01(d), 116.93(d), 110.86(d), 110.74(d), 109.08(s), 109.03(s), 44.95(t), 40.06(t), 16.97(q), 12.38(q);m/z: 227, 225(M^+), 186, 184, 146, 55.

N-(2-cyclohexenyl)aniline (3da): For spectral data see literature.[14,15]

N-(2-cyclohexenyl)-o-bromoaniline (3dc): $\nu_{max}(CCl_4)$ 3420, 2960, 1550, 1320,920; $\delta_H(DCCl_3)$ 6.1-7.2(5H, m), 5.6(2H, m), 4.1(1H, bb), 3.8(1H, m), 1.2-2(6H, m); $\delta_C(DCCl_3)$

143.80(s), 132.28(d), 130.23(d), 128.13(d), 127.71(d), 117.22(d), 111.58(d), 109.79(s), 47.71(d), 28.53(t), 24.89(t), 19.36(t);m/z: 253, 251(M^+), 172, 81.

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