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A STUDY ON THE AMINOMERCURATION-NUCLEOPHILIC DEMERCURATION OF CIS-CIS--1,5-CYCLOOCTADIENE; STEREOSELECTIVE SYNTHESIS OF 2,6-DISUBSTITUTED-9-AZA BICYCLO[3.3.1]NONANES

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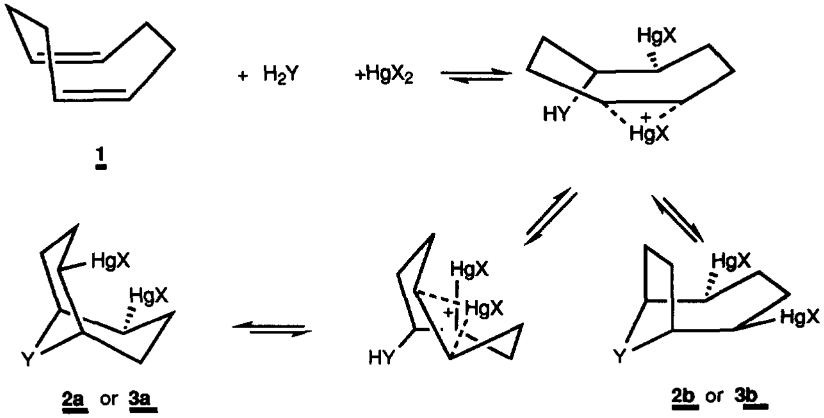
Abstract-*The aminomercuration of cis-cis-1,5-Cyclooctadiene with a series of mercury(II) salts followed by nucleophilic displacement of mercury by aromatic amines, water and nitrate ion has been studied. As a result, bicyclic triamines, aminoalcohols and nitrate esters have been obtained respectively in clean processes which occur under total stereoelectronic control by involvement of a tricyclic aziridium ion to afford a single stereoisomer in each case. The influence of the counter ion and the basicity of the amine on the tandem aminomercuration-demercuration is discussed.*

INTRODUCTION

On our continued work on the mercuration of alkenes with synthetic pourposes we have described in several papers the oxy- and aminomercuration reaction with different mercury(II) salts and the subsequent substitution of mercury in the resulting organomercurial for selected groups. When mercury(II) is removed creating a new C-H (reduction of the organomercurial) or C-C bond (reductive alkylation) the mercuration process is usually carried out with mercury(II) salts in which the anion has a relatively high nucleophilic character, such as acetate, and the reactions occur through free radicals.[1,2] Conversely the substitution of mercury for a second oxygen or nitrogen centered nucleophile requires the use of a mercury(II) salt containing an anion of low nucleophilic character to allow the ionic displacement of mercury.[3-7] Mercury has been substituted for halogens in many instances in a process that in some cases occurs with isomerization.[8,9] To get a better understanding of the reaction of displacement of mercury by nucleophiles, we have decided to perform a comparative study of the oxy- and aminomercuration of *cis,cis*-1,5-cyclooctadiene **1** with mercury(II) acetate, chloride, nitrate and tetrafluoroborate respectively and the subsequent nucleophilic



X= Cl, OAc, BF_4, NO_3

	Y
2	NAr
3	O

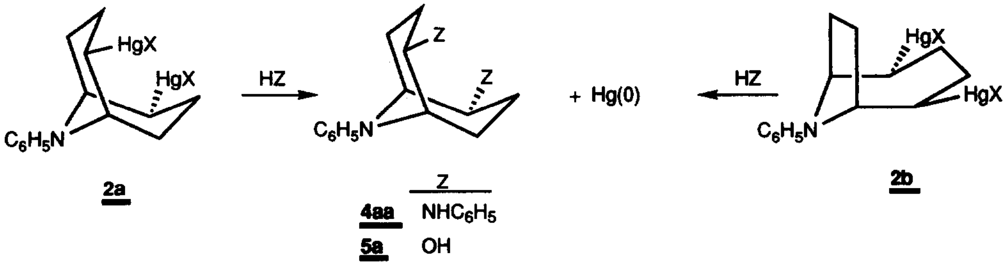
Scheme 1

demercuration of the resulting organomercurial. The selected reagents constitute an adequate framework for our purposes due to the cyclic carbon skeleton of the products allowing determination of the stereochemistry, and the possibility for the diene to afford two interconverting organomercurial regioisomers; all this including mercurations with covalent and ionic mercury(II) salts[10] (Scheme 1).

RESULTS AND DISCUSSION

The oxy- and aminomercuration of *cis,cis*-1,5-cyclooctadiene (1,5-COD) leads to the obtention of mixtures of regioisomeric mercurated oxa- or azabicyclononanes in a ratio which depends on the nature of the mercury(II) salt and also on the reaction conditions. While the aminomercuration reaction takes place to give the kinetically controlled adduct, i.e. 9-azabicyclo[4.2.1]nonane 2b or, under thermodynamic control, the 9-azabicyclo[3.3.1]nonane aminomercurial 2b,[10] the oxymercuration affords almost exclusively the more stable 9-oxabicyclo[3.3.1]nonane skeleton 3a .[11,12] Reactions are kinetically controlled when the mercurating species is a mercury(II) salt derived from a weak acid such as mercury(II) acetate and, conversely, thermodynamically controlled in mercurations with the covalent mercury(II) chloride. In the latter case the existence of free strong acid in the medium allows the thermodynamically controlled product to be obtained.

Mercury can be substituted by nucleophiles by heating the corresponding mercurials in the presence of amines, water, or alcohols. The ability of organomercurials to undergo this type of processes depends to a great extent upon the character of the C-Hg bond involved.



Scheme 2

Mercury(II) chloride mediated vicinal diamination of 1,5-COD. Two different mercuration reactions were carried out in acetonitrile or THF-sodium bicarbonate solution respectively in order to obtain the corresponding isomeric bicyclic aminomercurials 2a and 2b. The substitution of mercury for amine was performed by removal of the solvent followed by heating the resulting aminomercurial to 110°C in the presence of an excess of aniline for sixteen hours. The hydrogen chloride evolved in the aminomercuration in acetonitrile solution required neutralization prior to displacement by addition of sodium bicarbonate; otherwise the demercuration process was inhibited. The same bicyclic triamine 4aa was obtained as a single stereoisomer, as shown by ^{1}H- and ^{13}C-NMR analysis, independently of the regioisomer (2a or 2b) submitted to demercuration (Scheme 2, X=Cl).

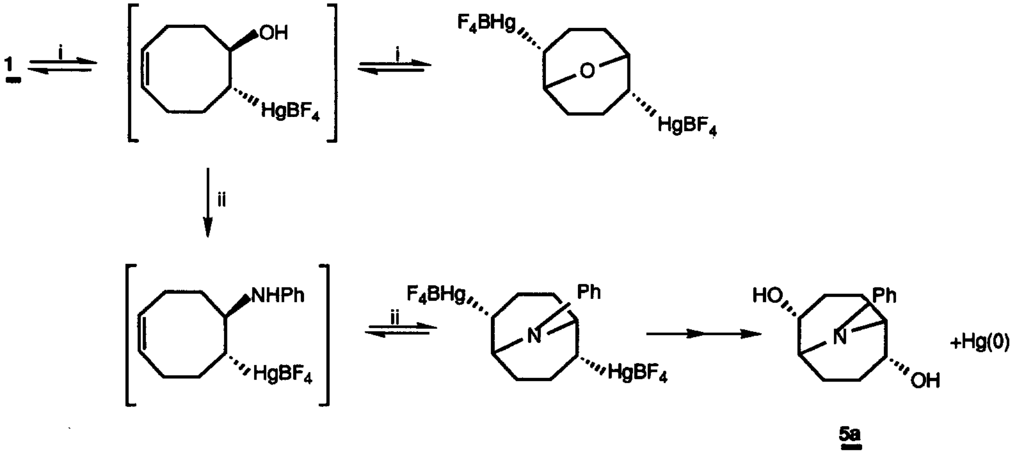
Mercury(II) acetate mediated vicinal diamination of 1,5-COD. The aminomercuration was carried out at room temperature to afford the kinetically controled regioisomer 2b as the only detectable (NMR) species. To perform the nucleophilic displacement of mercury(II) for amine it was necessary first to remove the solvent as well as keep the acetic acid generated in the course of the aminomercuration reaction, followed by heating the resulting residue in excess of amine at 110°C. In the oxidation process the rearrangement of the 9-azabicyclo[4.2.1]nonane 2b to the 9-azabicyclo[3.3.1]nonane skeleton 2a took place to afford the triamine 4aa as the only isolated product.

Mercury(II) tetrafluoroborate mediated vicinal oxyamination and diamination of 1,5-COD. The aminomercuration reaction at 0°C with this ionic salt, leads to the kinetically controlled regioisomer 2b. When the reaction mixture is allowed to reach the room temperature, mercury(0) precipitates spontaneously giving rise to products resulting from nucleophilic displacement of mercury. The aminomercuration was performed under different conditions in the presence or absence of water and the influence of the order of addition of the reagents determined. When water was mixed with 1,5-COD and mercury(II) tetrafluoroborate the oxymercuration reaction occured readily. However, addition of one equivalent of aniline to the oxymercuration mixture, resulted in the immediate substitution of water for amine followed by the precipitation of elemental mercury to give the corresponding oxidation product 5a (Scheme 3). Direct aminomercuration of 1 followed by addition of water and nucleophilic displacement of mercury gave a mixture of compounds 4aa and 5a (see run 5 in Table 1). The aminomercuration-demercuration under

Table 1. Mercury(II) Salt Mediated Vicinal Oxyamination and Diamination

Run	HgX_2(X)	Amine	Hg(II)/amine molar ratio	HZ or Z^-	Temperature °C	Reaction time h	Products and Molar Ratio [a,b]	Global Yield(%)[c]
1	Cl^d	$C_6H_5NH_2$	1/3	$C_6H_5NH_2$	110	16	4aa	26
2	Cl^e	$C_6H_5NH_2$	1/3	$C_6H_5NH_2$	110	16	4aa	38
3	AcO	$C_6H_5NH_2$	1/3	$C_6H_5NH_2$	110	2	4aa	45
4	BF_4	$C_6H_5NH_2$	1/0.5	H_2O^f	80	8	5a	40
5	BF_4	$C_6H_5NH_2$	1/0.5	$H_2O,C_6H_5NH_2{}^g$	80	8	4aa(0.4)/5a(0.6)	64
6	BF_4	$C_6H_5NH_2$	1/1.5	$C_6H_5NH_2$	80	8	4aa	61
7	NO_3	$C_6H_5NH_2$	1/2	NO_3^-	80	8	6aa	70
8	NO_3	$C_6H_5NH_2$	1/0.5	NO_3^-	80	8	6aa(o.45)/6ab(0.15)/ 6ac(0.3)/7bc(0.1)	75
9	NO_3	$C_6H_5NH_2$	1/0.5	NO_3^-, H_2O^h	80	8	6aa	69
10	NO_3	p-$NO_2C_6H_5NH_2$	1/0.5	NO_3^-	80	16	6ac(0.7)/7bc(0.3)	48

[a] All compounds gave satisfactory elemental analysis. [b] Molar ratio in parentheses was determined by ^{1}HNMR analysis of the reaction mixture. [c] Based on mercury(II) salt. [d] The aminomercurial was obtained under thermodynamic conditions.[10] The aminomercurial was obtained under kinetic conditions.[10] [f] Water was added 15min before aniline. [g] Aniline was added before water. [h] Water was added before heating.



Reactives: i) H_2O, $HgBF_4$; ii) $PhNH_2$, $Hg(BF_4)$

Scheme 3

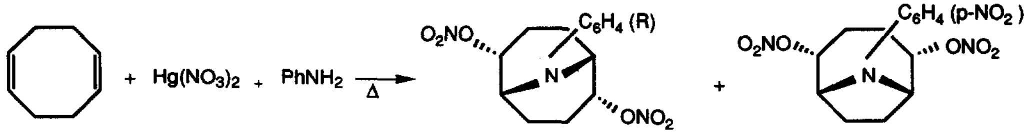
anhydrous conditions gave compound 4aa in 61% yield as a single product as expected.

Mercury(II) nitrate mediated vicinal oxyamination of 1,5-COD. The aminomercuration of 1,5-COD with mercury(II) nitrate in presence of aniline and THF as solvent at room temperature gave a mixture of the isomeric aminomercurials 2a and 2b in a ratio 0.76:0.19 and these were characterized after reduction with sodium borohydride. The use of anhydrous mercury(II) nitrate in dry THF with an excess of aniline or use of the hydrated salt in THF/water, either a stoichiometric amount of amine or an excess, did not induce any change in the course of the aminomercuration. The nucleophilic displacement of mercury promoted by heating of the β-aminoalkylmercury(II) nitrate salt follows a different course compared with the one observed in the case of the previous aminomercurials. When the mixture of isomeric aminomercurials 2a ($X = NO_3$) and 2b ($X = NO_3$) was heated at 80°C the stereospecific formation of a single dinitrate 6aa was observed to take place with good yield (75%). It is worth mentioning that no competition was observed from water or the free amine when present with the nitrate ion in the nucleophilic displacement of mercury. This would be expected for the nitrate ion/water pair but not for the nitrate ion/amine couple. However, since nitric acid is evolved in the course of the aminomercuration the excess of amine will be present as a nitrate salt and in this form will not able to exhibit any

Table 2. NMR Spectral Data (δppm, TMS) for compounds **4aa**, **5a**, **6aa**, **6ab**, **6ac**, and **7bc**

Compound	^{1}H-NMR	^{13}C-NMR	M^{+}
4aa	1.7-2.1(m,8H), 3.7(m,4H), 6.6-7.2(m,15H)	148.54(s), 146.52(s), 129.97(d), 129.72(d), 117.98(d), 117.45(d), 113.68(d), 113.45(d), 51.49(d), 48.99(d), 28.49(t), 21.34(t)	383
5a	1.7-2.2(m,8H), 3.8(m,2H), 4.0(m,4H), 6.8-	149.00(s), 129.34(d), 116.56(d), 113.58(d), 67.93(d), 52.81(d), 29.97(t), 25.09(t)	233
6aa	1.8-2.2(m,8H), 4.2(m,2H), 5.3(m,2H), 6.8-7.4(m,4H)	147.17(s), 130.08(d), 119.44(d), 114.44(d), 79.04(d), 48.47(d), 24.01(t), 21.71(t)	323
6ab	1.9-2.2(m,8H), 3.6(m,2H), 5.3(m,2H), 7.0-7.7(m,4H)	141.76(s), 137.27(s), 133.88(d), 127.00(d), 121.41(d), 120.01(d), 78.14(d), 52.09(d), 23.78(t), 22.05(t)	368
6ac	2.0-2.3(m,8H), 4.4(m,2H), 5.25(m,2H), 6.9 (d,2H), 8.2(d,2H)	151.99(s), 139.24(s), 126.65(d), 112.79(d), 78.27(d), 48.69(d), 23.69(t), 21.79(t)	368
7bc	2.0-2.3(m,8H), 4.8(m,2H), 5.4(m,2H), 6.8 (d,2H), 8.2(d,2H)	149.15(s), 139.24(s), 127.14(d), 110.80(d) 78.91(d), 56.74(d), 23.49(t), 23.41(t)	368

nucleophilic character. When reactions are carried out in excess of amine and the mixture neutralized on work-up and then purified by column chromatography in silica gel, compound 6aa undergoes partial displacement of the nitrate by amine giving the corresponding triamine 4aa along with the nitrate ester 6aa. When aminomercurations are performed under anhydrous conditions with the stoichiometric quantity of aniline, nitration of the aromatic ring is observed to occur in the *ortho* or *para* positions simultaneously to the substitution of mercury for nitrate ion. In these conditions this latter reaction is not regiospecific as shown by the obtention of four nitrate esters 6aa, 6ab, 6ac, and 7bc, (Scheme 4).

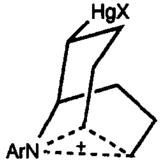


	R
6aa	H
6ab	o-NO_2
6ac	p-NO_2

7bc

Scheme 4

From the above results it can be deduced that both types of aminomercurials 2a and 2b afford in the oxidative demercuration process a single type of product with the skeleton of *cis*-2,6-disubstituted 9-azabicyclo[3.3.1]nonane. These transformations can be rationalized by considering anchimeric assistance by the lone electron pair of the bridge amino group for the elimination of elemental mercury through an intermediate aziridium ion 8. Confirmation of this hypothesis is found in the different course of the reaction when the aminomercuration-demercuration is performed with mercury(II) nitrate under anhydrous conditions. This situation leads to the nitration of the aromatic amine *prior* to the mercuration taking place. In this case the



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basicity of the amine lone pair becomes highly diminished in the aminomercurials 2a [Ar=$C_6H_4(p\text{-}NO_2)$] and 2b [Ar=$C_6H_4(p\text{-}NO_2)$] and, hence, the highly unstable intermediate aziridine 8 formed in this case will undergoes a less selective opening by the subsequent nucleophilic attack giving rise only in this case to a mixture of the regioisomers 6ac and 7bc. To ascertain the proposed reaction path in a test experiment 1,5-COD was mercurated with mercury(II) nitrate and para-nitroaniline in THF solution affording after heating the same mixture of regioisomers 6ac and 7bc in a similar ratio.

Electron-attracting groups attached to position 2,6- in the 9-azabiciclo[3.3.1]nonane skeleton have been found to be very labile towards nucleophilic substitution. Thus, products 5a and 6aa on attempted purification by column chromatography using acid silica-gel undergo substitution of the -OH or $-ONO_2$ groups respectively by residual aniline giving in all cases the triamine 4aa as the product. This reaction once more indicates the enhancement of reactivity of these bicyclic skeleta as a consequence of stereoelectronic factors.

The complexity of the ^{1}H-NMR spectra even at 500 MHz made the measurement of coupling constants difficult. For this reason compound 6ab was crystallized and the X-ray structure determined in order to confirm the structural assigment made based on NMR data, (Figure 1).

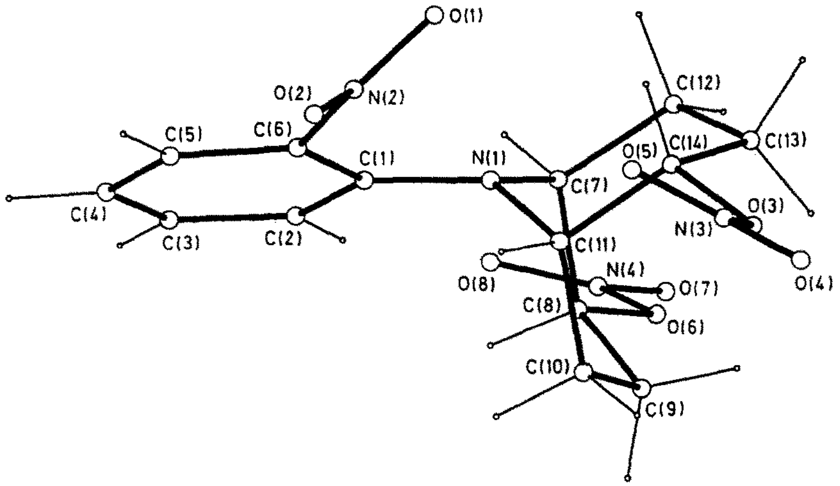

Figure 1. X-Ray diffraction structure of compound 6ab

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EXPERIMENTAL

X-ray Crystallographic Determination of *<u>trans</u>-2,6-dinitrato-N-phenyl-9-azabicyclo*[*3.3.1*]*nonane* *<u>6ab</u>:*

Yellow crystal, $C_{14}H_{16}N_4O_8$, 0.33x0.13x0.10 mm size. M_r= 386.30, orthorhombic, space group $P2_12_12_1$, a=8.784(7), b=10.095(2), c=18.093(4) Å, V=1604(1) $Å^3$, Z=4, D_x=1.52 Mg/m^3. MoKα radiation used with a graphite (λ= 0.71073 Å), Z=4, D_x=1.52 Mg/m^3. MoKα radiation used with a graphite crystal monochromator on a Enraf Nonius CAD4 single crystal diffractometer reflections with 10°<θ<15°. Space group $P2_12_12_1$ from the systematic absences. 5061 reflections measured, hkl range (-12, 0, 0) to (12, 14, 25), theta limits (0°<θ<30°). w-2θ scan technique and a variable scan rate with a maximun scan time of 60s per reflection. Intensity checked by monitoring three standard reflections every 60 minutes. Final drift correction factors between 0.98 and 1.00. Profile analysis was performed on all reflections;[13,14] semiempirical absorption correction was applied, using ψ scans,[15] μ(MoKα)= 1.19 cm^{-1} (correction factors in the range 0.98 to 1.00). Symmetry equivalent reflections averaged, R_{int}= $\Sigma(I-<I>)/\Sigma I$% 0.031, resulting in 4669 unique reflections of which only 1419 were observed with $I>3\sigma(I)$. Lorentz and polarization corrections applied and the data reduced to $|F_o|$-values. Structure solved by Direct Methods, using the program SHELX86.[16]

Isotropic least-squares refinement, using SHELX76,[17] converged to R= 0.089. At this stage additional empirical absorption correction was applied.[18] Maximum and minimum absorption correction factors, respectively, 1.10 and 0.36. Further anisotropic refinements followed by a Difference Fourier synthesis allowed the location of some hydrogen atoms, the rest of H-atoms were geometrically placed.

During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. All hydrogens were refined isotropically riding on their parent atoms from his geometrically idealized positions. The absolute configuration was checked with BIJVOET,[19] resulting B=0.781 for 10 pairs.The final conventional agreement factors were R= 0.034 and R_w= 0.033

for the 1419 'observed ' reflections and 260 variables. The function minimized was $\Sigma w(F_o-F_c)^2$, $w=1/(\sigma^2(F_o) + 0.00015\ F_o^2)$ with $\sigma(F_o)$ from counting statistics. The maximum shift over error ratio in the last full matrix least-squares cycle was less than 0.050. The final Difference Fourier map showed no peaks higher than 0.17 e/Å^3 and deeper than -0.19 e/Å^3. Atomic scattering factors were taken from the International tables for X-ray Crystallography (1974).[20] The plot was made with the PLUTO program.[21] Geometrical calculations were made with PARST.[22] Distances and angles are normal. All suplementary crystallographic data are available on request from the Cambridge Crystallographic Data Centre.Molecular geometry data are collected in Table 3. Figure 2 shows the atomic numbering scheme.[23]

^{1}H and ^{13}C-NMR spectra were recorded in a Varian Gemini 200 NMR and a Varian-XL 500 NMR spectrometers. I.r. spectra were recorded in a Perkin Elmer Model 843 i.r. spectrometer. Mass spectra were measured on a Hewlett Packard Model 5930 A mass spectrometer. 1,5-COD, mercury(II) salts (acetate, chloride and nitrate) and aromatic amines were commercially available and were used as received. Mercury(II) tetrafluoroborate was prepared as previously reported.[3] For TLC and column separations silica gel (Merck) was used with toluene-hexane-diethylamine (75:15:10) as eluant.

Mercury (II) chloride mediated vicinal diamination of 1,5-COD: a)2,6-di(chloromercury)-N-phenyl-9-azabicyclo[3.3.1]nonane (6,7g, 10mmol) was prepared as previously reported[10] in acetonitrile solution. Solvent was removed at reduced pressure and the residue dissolved in aniline (10 mmol). The solution was heated under an inert atmosphere at 110°C for 16h. The mercury(0) which precipitated and was filtered off, the excess of aniline was evaporated under reduced pressure and the oily residue was purified by column chromatography on silica-gel using toluene:hexane:diethylamine (75:15:10) as eluant to give **4aa** (1.0g, 26%). *trans*-2,6-diphenylamino-N-phenyl-9-azabicyclo[3.3.1]nonane **4aa** ($C_{26}H_{29}N_3$): elemental analysis Calc: C, 81.46%; H, 7.57%; N, 10.97%. Found: C, 81.42%; H, 7.59%; N, 10.96%; ν_{max}(CCl$_4$) 3420, 3040, 3020, 2920, 1600, 1500, 1310, 1260, 710, 650 cm^{-1}.

b)2,5-di(chloromercury)-N-phenyl-9-azabicyclo[4.2.1]nonane (6.7g, 10 mmol) was prepared as previously reported[10] in THF solution. Solvent was removed under reduced pressure and the residue dissolved in aniline. The solution was heated under an inert atmosphere at 110°C for 16h. The work-up procedure was analogous to that described previously and the NMR spectrum of the oily residue showed this to be <u>4aa</u> (1.5g, 38%).

Mercury(II) acetate mediated vicinal diamination of 1,5-COD
To a solution of mercury(II) acetate (3.2g, 10mmol) and aniline (1.9mL, 20mmol) in THF (30mL), was added 1,5-COD (1.3mL, 10mmol) and the mixture stirred for 8h. The solvent and the acetic acid evolved were removed under reduced pressure and the reaction mixture was subsequentlyed heated to 110°C for 2h. The work-up procedure was analogous to that described previously. The residue was chromatographed to yield <u>4aa</u> (0.86g, 45%).

Mercury(II) tetrafluoroborate mediated vicinal oxyamination
To a solution of mercury(II) tetrafluoroborate (3.75g, 10mmol) and water (0.4mL, 20mmol) in THF (20mL), was added 1,5-COD (1.3mL, 10mmol) and the mixture stirred for 15min. After addition of aniline (0.45mL, 5mmol) the reaction mixture was heated to 80°C for 8h. The work-up procedure was analogous to that described previously. The residue was chromatographed to yield <u>5a</u> (0.47g, 40%).

<u>trans</u>-2,6-dihidroxi-N-phenyl-9-azabicyclo[3.3.1]nonane <u>5a</u> ($C_{14}H_{19}NO_2$): elemental analysis Calc: C, 72.10%; H, 8.15%; N, 6.01%. Found: C, 71.90%; H, 8.21%, N, 5.98%; (m.p.:155°C) ; $\nu_{max}(CCl_4)$ 3300, 2950, 1600, 1500, 1460, 1050, 970, 900, 700, 620 cm^{-1}.

Mercury(II) tetrafluoroborate mediated vicinal oxy- and diamination
To a solution of mercury(II) tetrafluoroborate (3.75g, 10mmol) and aniline (0.45mL, 5mmol) in THF (20mL), 1,5-COD (1.3mL, 10mmol) was added and the mixture stirred for 15 min. After addition of water (0.4mL, 20mmol) the reaction mixture was heated at 80°C for 8h. The work-up procedure was analogous to that described previously. The residue was purified by preparative column chromatography (silica gel; toluene:hexane:diethylamine (75:15:10) to yield a mixture of compounds <u>4aa</u> and <u>5a</u> with a 0.4/0.6 molar ratio (0.93g, 64%).

Mercury(II) tetrafluoroborate mediated vicinal diamination of 1,5-COD
Mercury(II) tetrafluoroborate (3.75g, 10mmol) and aniline (1.35mL, 15mmol) was added to a solution of 1,5-COD (1.3mL, 10mmol) in THF (20mL). The reaction mixture was heated at 80°C for 8h. The work-up procedure was analogous to that described above. The residue was chromatographed to yield <u>4aa</u> (1.2g, 61%).

Mercury(II) nitrate mediated vicinal oxyamination of 1,5-COD (Table 1, runs 7-10).

To a solution of 1,5-COD (2.6mL, 20mmol) in THF (40mL) was added the corresponding amine and $Hg(NO_3)_2$ (6.5g, 20mmol) (in the molar ratio shown in Table 1) and the reaction mixture stirred at 80°C for 8h to 16h. The mercury(0) which precipitated and was removed by filtration. The subsequent work-up procedure was analogous to that described previously. The residue was purified by preparative column chromatography (silica gel; toluene:hexane:diethylamine (75:15:10)) to yield the nitrate esters **6aa**, **6ab** (m.p.: 132°C), and a mixture of 6ac and 7bc in the molar ratio shown in Table 1. In run 9 water (10 mmol) was added to the reaction mixture before heating.

trans-2,6-dinitrato-N-phenyl-9-azabicyclo[3.3.1]nonane **6aa** ($C_{14}H_{17}N_3O_6$): elemental analysis Cal: C, 52.01%, H, 5.26%, N, 13.00%, Found: C, 51.98%; H, 5.21%; N, 12.88% ; ν_{max} 2954, 1640, 1596, 1496, 1307, 1270, 961, 847 cm^{-1}.

trans-2,6-dinitrato-N-o-nitrophenyl-9-azabicyclo[3.3.1]nonane **6ab** : ($C_{14}H_{16}N_4O_8$): elemental analysis Calc: C, 45.65%; H, 4.20%; N, 11.41%. Found: C, 45.20%, H, 4.21%, N, 11.00%; m.p.= 132°C; ν_{max} 2928, 1650, 1640, 1496, 1272, 846 cm^{-1}.

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