*Tetrahedron* Vol. 40, No. 7, pp. 1199 to 1204, 1984

# THE QUESTION OF THE REVERSIBILITY IN THE AMINOMERCURATION OF OLEFINS. SYNTHESIS OF N-ARYL-9-AZABICYCLO[4.2.1] AND [3.3.1] NONANES BY AMINOMERCURATION OF *cis-cis*-1,5-CYCLOOCTADIENE

José Barluenga, Julia Pérez-Prieto, Ana M. Bayón and Gregorio Asensio
Departamento de Química Orgánica. Facultad de Química, Universidad de Oviedo. Oviedo, Spain
Spain

(*Received in the UK* 13 *May* 1983)

**Abstract**—The aminomercuration of olefins is found to be a reversible or irreversible process depending on the nature of the mercury(II) salt employed. This is in clear contrast with the mechanism of oxymercuration reactions. A selective synthesis of the title compounds is described by kinetically or thermodinamically controlled aminomercuration of *cis-cis*-1,5-cycloctadiene.

The mechanism and utility in organic synthesis[1] of oxymercuration reactions have been studied in deep and shown to take place via a reversible process, through the formation of an ionic intermediate. For instance, this can be concluded by the study of transoxymercuration and deoxymercuration reactions,[2] and also by the spectroscopic detection of mercurinium cations.[3] By contrast the mechanism of the synthetically useful aminomercuration processes has received comparatively little attention. Moreover, some results might be obscured by later rearrangements in the reduction step[4] and others, such as the different rate of aminomercuration observed with the use of various mercury(II) salts have been found to be contradictory.[5,6] On the other hand, the question of the reversible or irreversible character of the aminomercuration reaction has not arisen so far.

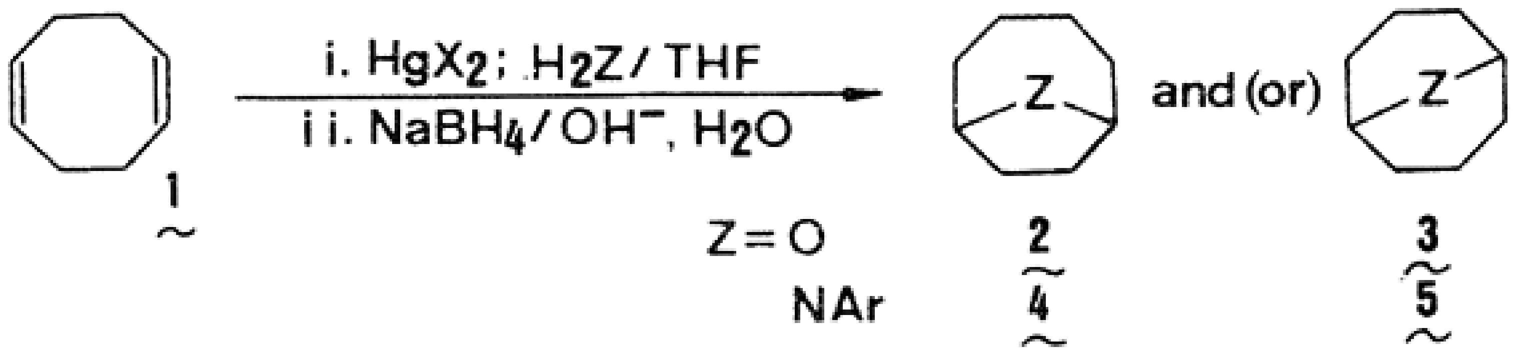
The mercuration-demercuration reaction of *cis-cis*-1,5-cyclooctadiene **1** has been widely studied as an insight to the synthesis of 9-oxa- and 9-azabicyclononane derivatives.[7–12] However, the results of the reaction have been often the subject of some controversy, since the two isomeric bicyclo[3.3.1]- and [4.2.1]nonanes can be formed after the sodium borohydride reduction (Scheme 1) depending on the reaction conditions in the mercuration step. In addition, the differentiation between these two types of skeletal arrangements was difficult until the introduction of $^{13}$C NMR.[13]

It was likely that the alternative formation of these bicyclic skeletons could result from a kinetically or thermodynamically controlled mercuration process and, hence, we felt that the study of the mercuration of *cis-cis*-1,5-cyclooctadiene **1** in the presence of primary aromatic amines would provide the appropriate framework to determine the conditions in which the aminomercuration is a reversible process.

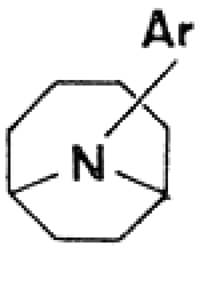
For the above reasons, we wish to report now our detailed study on the reaction of *cis-cis*-1,5-cyclooctadiene with aromatic amines in the presence of a series of mercury(II) salts by using different molar ratios and solvents which enables to clarify the question of the reversibility of the aminomercuration of olefins. As a result, we propose a mechanism for the aminomercuration process and develop a regioselective synthesis of N-aryl-9-azabicyclo[3.3.1]-**5** and N-aryl-9-azabicyclo[4.2.1] nonane **4** respectively.

## RESULTS AND DISCUSSION

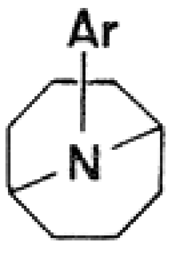
Calculated strain energies[14] indicate that bicyclo[3.3.1]nonane is more stable than bicyclo[4.2.1]nonane by 47.57 kJ mol$^{-1}$. Since the substitution of the amine nitrogen for the sp$^3$ hybridized bridge carbon should not reverse the stability order, we assume that under thermodynamic control, i.e. in a reversible aminomercuration of *cis-cis*-1,5-cyclooctadiene **1**, the [3.3.1] isomer **8** will predominate. The cyclization reaction will proceed in two



Scheme 1.



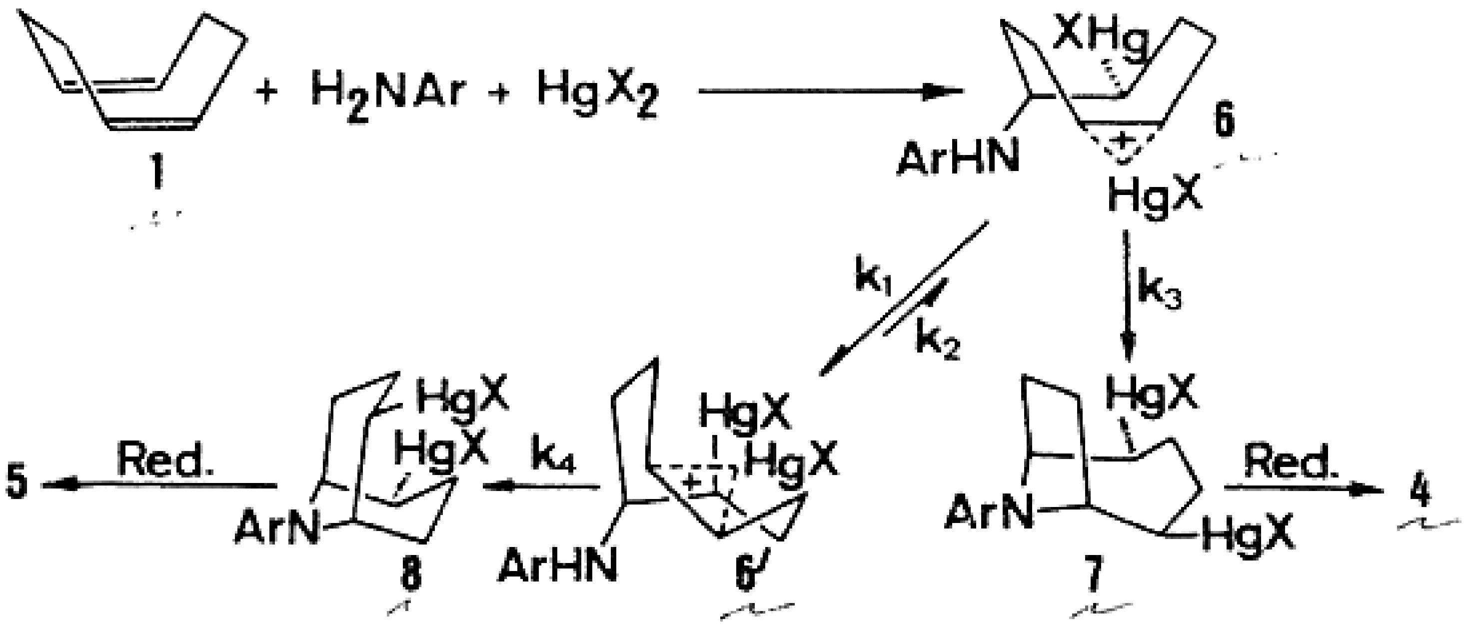
| | Ar | |
|---|---|---|
| **4a** | $C_6H_5$ | **5a** |
| **4b** | (p)$CH_3C_6H_4$ | **5b** |
| **4c** | (p)$ClC_6H_4$ | **5c** |
| **4d** | (p)$BrC_6H_4$ | **5d** |
| **4e** | (m)$CH_3C_6H_4$ | **5e** |



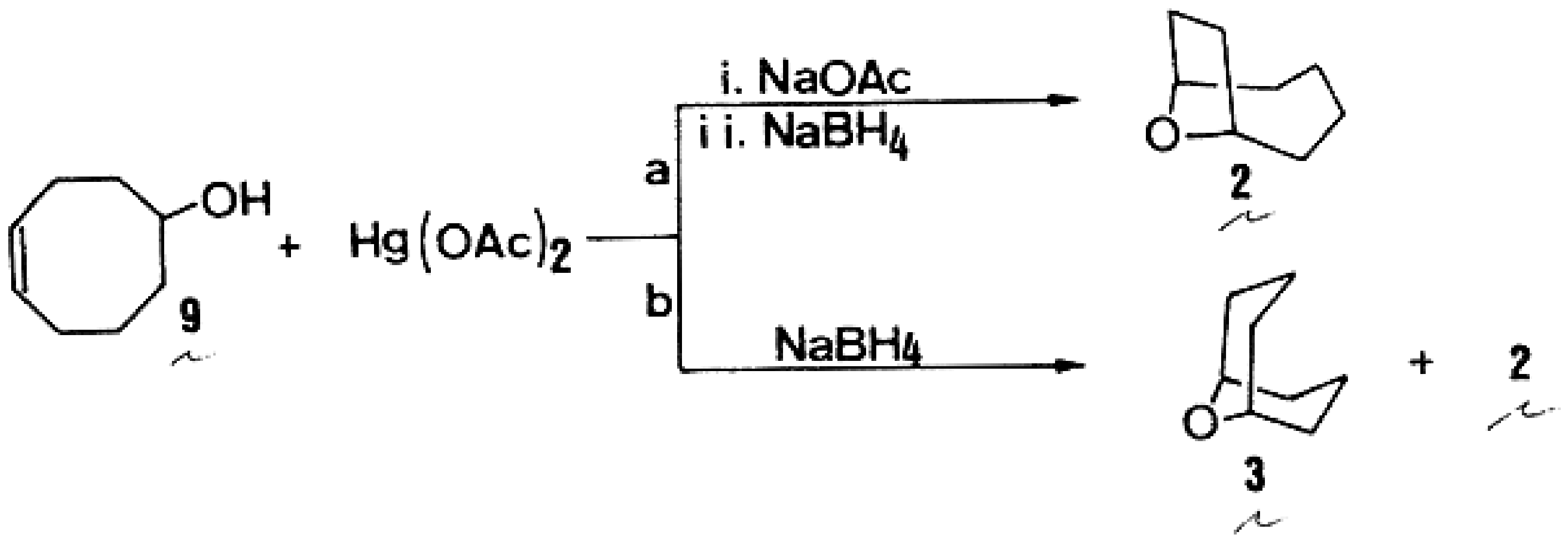
steps, the latter of them being the fast intramolecular aminomercuration of the second double bond.[15] For geometric reasons, the formation of the transition state which leads to the aminomercurial **7** is expected to be kinetically favourable as it does not require any conformational change and hence, this isomer should be obtained in reactions carried out under kinetic control (Scheme 2). Results consistent with this analysis are found when 4-cycloocten-1-ol **9** is treated with mercury(II) acetate in the presence of sodium acetate (Scheme 3, Path a) which leads to 9-oxabicyclo[4.2.1]nonane **2** uncontaminated by the 1,5-epoxide isomer **3**.[1] In the absence of sodium acetate (Scheme 3, Path b) a mixture of both the 1,4- **2** and the 1,5- epoxide **3** isomers is obtained.[1] A similar result is obtained when *cis*, *cis*-1,5-cyclooctadiene is treated with mercury(II) acetate in water/THF solution. In the presence of sodium acetate the mercuration was complete in 40 min and a 0.55/0.45 mixture of the oxymercurials **10** and **12** was obtained (Scheme 4). When the oxymercuration mixture was stirred for 24 additional hours the **10**:**12** isomer ratio found was 0.47/0.53. Thus, the isomerization **10**→**12** is a very slow process in weak alkaline media.

The mercuration with mercury(II) acetate in absence of sodium acetate was complete in about 30 min and also a 0.55/0.45 **10**:**12** isomer ratio was then found. When the oxymercuration mixture was allowed to stand for 24 hr at room temperature a nearly total conversion of **10** into **12** was observed (Scheme 4). The mercuration with mercury(II) nitrate afforded **12**(as $NO_3$ derivative) as a single isomer in only a few seconds. The progress of the oxymercuration reaction was followed in all instances by $^{13}C$ NMR. Reactions were considered to be compleat when no yellow precipitate of mercury(II) oxide was obtained upon treatment of a sample from the reaction mixture with 1N potassium hydroxide.

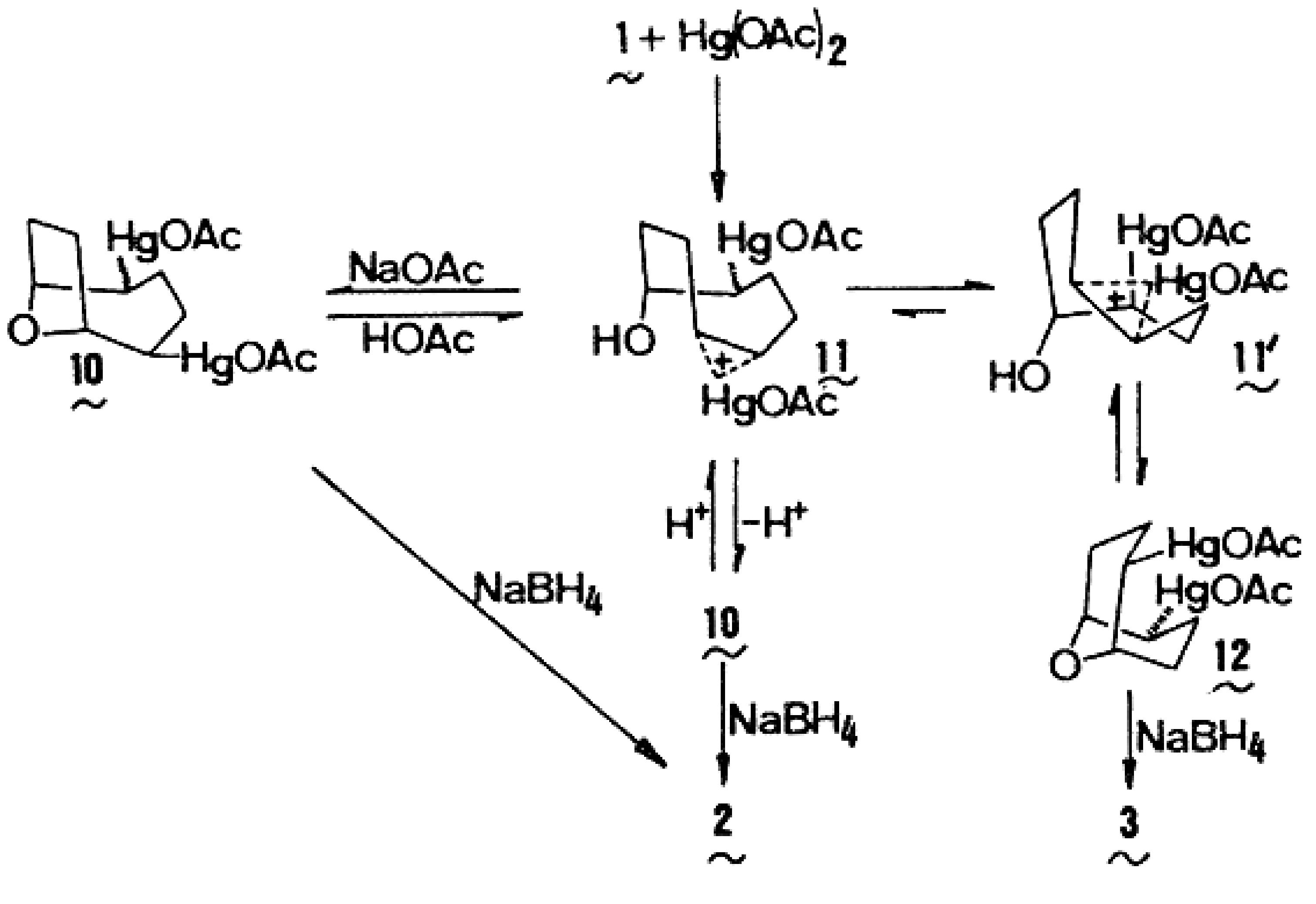
In contrast, aminomercuration of **1** with mercury(II) acetate (Scheme 2, X = OAc) leads, independently of the reaction time or temperature, only to the 1,4-azabicycloalkane **4** and less than 10% of the 1,5-isomer **5**.



Scheme 2.



Scheme 3.



Scheme 4.

The different course of oxy- and aminomercuration reactions under similar conditions suggests that the acetic acid generated in the mercuration, promotes the rearrangement of the kinetic oxymercuration adduct **10** through the equilibrium between **11** and **11′** which implies the acid catalyzed deoxymercuration of **10** (Scheme 4).

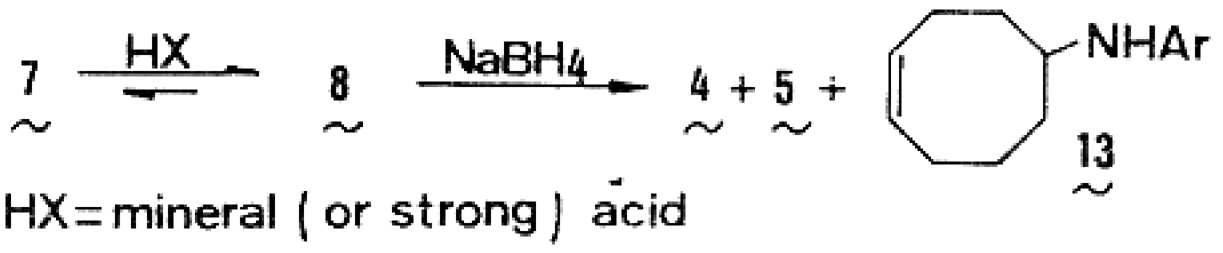
On the contrary, acetic acid fails to promote the deaminomercuration of the adduct **7** (X = OAc). Then, it is inferred that aminomercuration with mercury(II) acetate appears to be an irreversible process. The sodium borohydride reduction of **7** affords the corresponding N-arylazabicyclo [4.2.1]nonanes **4** in good yields[16] (Scheme 2). As stated above, **4** is contaminated by small amounts of the 1,5-isomer **5**, probably from reduction of the adduct **8**. This suggests that the rate constant $k_1$ for the conversion of **6** into **6′** is small if compared with $k_3$, the intramolecular quenching of the mercurinium ion in **6** to yield the aminomercurial **7**. From our results we cannot rule out the possibility of a minor rearrangement of **7** in the reduction step which would account for the formation of **5**. In any case this would lead also to the conclusion that $k_3 > k_1$ since **8** would not be derived from the mercuration step.

The use of mercury(II) salts of mineral acids leads after sodium borohydride reduction to 1,5-azabicyclo **5** by rearrangement of the kinetic aminomercurial **7** initially formed (see Table 1). Mercury(II) nitrate, tetrafluoroborate, trifluoroacetate, bromide and chloride were tested as mercurating agents, and it was found that the more covalent the mercury salt the more effectively it promotes the rearrangement. The best conditions for the synthesis of the [3.3.1]azabicyclic systems **5** are the use of mercury(II) chloride in a polar solvent, i.e. acetonitrile with a 1 : 1 amine/mercury(II) salt molar ratio and a reaction time of 48 h at room temperature. Shorter reaction times lead in all the cases studied to the formation of mixtures of both isomers **4** and **5**. This suggests that the transformation **7**→**8** is favored by both the use of covalent mercury(II) salts[17] and the presence of a strong acid responsible for the existence of **7** in the protonated form. Since aminomercurations were carried out in the presence of an excess of olefin, it can be deduced that the conversion **7**→**8** does not imply a transaminomercuration but a monodeaminomercuration reaction.[18]

Compounds **8**(X = Cl) can be alternatively synthesized by rearrangement of the isolated aminomercurials **7** (X = Cl) when these are treated with two equivalents of concentrated hydrochloric acid in DMF solution at room temperature for 48 h. Aminomercurial **7**(X = Cl) are prepared in nearly cuantitative yield by aminomercuration of 1,5-COD with mercury(II) acetate in dioxane followed by anionic exchange with a solution of potassium chloride in water. By contrast, when aminomercurials **7** (X = Cl) were treated with acetic acid under the same conditions as described above, no isomerization **7**→**8** could be detected to take place after sodium borohydride reduction (Scheme 5).

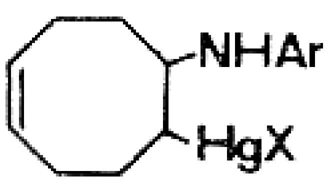
The rate of aminomercuration increases with the ionic character of the mercury salt and the polarity of the solvent but the extent to which the rearrangement **7**→**8** takes place largely depends on the temperature and reaction time (see Table 1). For instance, with mercury(II) nitrate at temperatures of 0° or below in DMF nearly complete conversion to the organomercurial is achieved, but after 15 minutes the product found after reduction was the 1,4-azabicyclic system **4** contaminated by only minor amounts of the 1,5-isomer **5**. At room temperature the isomerization takes place much faster but a part of the mercury is reduced to the elemental state in the course of the reaction and precipitates. This side reaction becomes more important as the coordinative ability of the solvent decreases, that is, with the localization of positive charge on the mercury. The same trend is observed for other ionic mercury(II) salts such as tetrafluoroborate or trifluoroacetate.

After sodiumborohydride reduction of the aminomercuration mixture $\delta,\gamma$-unsaturated amines **13** (Scheme 6) were always detected and isolated in variable yield.

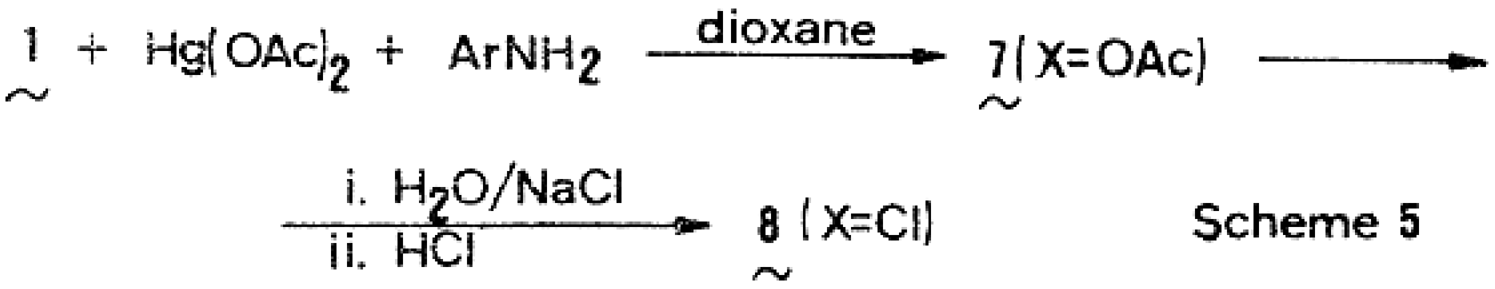


Scheme 6.

The largest insaturated amine/bicyclic compound ratio was found in mercurations with mercury(II) chloride while the amount of **13** is negligible when mercury(II) acetate is used. This is attributed to the existence of unsaturated aminomercurial **14** in equilibrium with the bicyclic species **7** and **8** in a quantity which differs with the nature of the anion associated with mercury, and for the strength of the acid present in the reaction mixture. An alternative route to compounds **13** could be the partial deaminomercuration of **7** and/or **8** in the reduction step. Since the formation of **13** from isolated **7** (X = OAc, Ar = $C_6H_5$) is almost completely avoided by the use of the appropriate homogeneous reduction conditions,[20] it is likely that **13** (Ar = $C_6H_5$) derives from the aminomercuration process itself and not from deaminomercuration of **8** (X = Cl) in the reduction step. The nature of the anion should not affect the course of reduction since this is carried out in alkaline media and hence, previous anionic exchange for the hydroxy group is expected to occur.[21]



**14**



Scheme 5.

Table 1. Aminomercuration-reduction of *cis-cis*-1,5-cyclooctadiene with aromatic amines

| Run | $ArNH_2$ (Ar) | $HgX_2$ (X) | Amine/Hg(II) molar ratio | Solvent | Temperature °C | Reaction time h | Products[a] **4**,**5**,**13** | **4**/**5**/**13** Ratio[b] | **4**+**5** Yield(%)[c] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | Cl | 2 | THF | 25 | 1 | **a** | 0.28/0.53/0.19 | 9.5 |
| 2 | $C_6H_5$ | Cl | 2 | THF | 25 | 6 | **a** | 0.25/0.56/0.19 | 28.0 |
| 3 | $C_6H_5$ | Cl | 2 | THF | 25 | 24 | **a** | 0.21/0.63/0.16 | 39.0 |
| 4 | $C_6H_5$ | Cl | 2 | THF | 25 | 48 | **a** | 0.17/0.66/0.17 | 42.0 |
| 5 | $C_6H_5$ | Cl | 2 | DMF | 25 | 1 | **a** | 0.64/0.27/0.09 | 34.5 |
| 6 | $C_6H_5$ | Cl | 1 | $THF/H_2O(3:1)$ | 25 | 48 | **a** | – /1.00/ – | 64.0 |
| 7 | $C_6H_5$ | Cl | 1 | $CH_3CN$ | 25 | 48 | **a** | – /1.00/ – | 64.0 |
| 8 | $C_6H_5$ | Cl | 1 | THF(anh) | 25 | 48 | **a** | – /1.00/ – | 20.0 |
| 9 | $p-CH_3-C_6H_4$ | Cl | 1 | $CH_3CN$ | 25 | 48 | **b** | – /1.00/ – | 60.0 |
| 10 | $p-Cl-C_6H_4$ | Cl | 1 | $CH_3CN$ | 25 | 48 | **c** | – /1.00/ – | 68.0 |
| 11 | $p-Br-C_6H_4$ | Cl | 1 | $CH_3CN$ | 25 | 48 | **d** | – /1.00/ – | 51.2 |
| 12 | $m-CH_3-C_6H_4$ | Cl | 1 | $CH_3CN$ | 25 | 48 | **d** | – /1.00/ – | 73.0 |
| 13 | $C_6H_5$ | AcO | 2 | THF | 25 | 6 | **e** | 0.85/0.15/ – | 36.0 |
| 14 | $C_6H_5$ | AcO | 2 | THF | 25 | 24 | **a** | 0.85/0.15/ – | 70.0 |
| 15 | $C_6H_5$ | AcO | 2 | THF | 25 | 96 | **a** | 0.85/0.15/ – | 78.0 |
| 16 | $p-CH_3-C_6H_4$ | AcO | 2 | THF | 25 | 24 | **a** | 0.85/0.15/ – | 80.0 |
| 17 | $p-Cl-C_6H_4$ | AcO | 2 | THF | 25 | 24 | **b** | 0.85/0.15/ – | 79.0 |
| 18 | $p-Br-C_6H_4$ | AcO | 2 | THF | 25 | 24 | **c** | 0.85/0.15/ – | 78.0 |
| 19 | $m-CH_3-C_6H_4$ | AcO | 2 | THF | 25 | 24 | **d** | 0.85/0.15/ – | 82.0 |
| 20 | $C_6H_5$ | $NO_3$ | 2 | THF[d] | 25 | 2 | **e** | 0.76/0.19/0.05 | 45.0 |
| 21 | $C_6H_5$ | $NO_3$ | 2 | DMF[e] | 25 | 6 | **a** | 0.60/0.40/ – | 83.0 |
| 22 | $C_6H_5$ | Br | 2 | THF | 25 | 24 | **a** | 0.31/0.55/0.14 | 30.0 |
| 23 | $C_6H_5$ | $NO_3$ | 2 | DMF | 0 | 0.25 | **a** | 1.00/ – / – | 50.0 |
| 24 | $C_6H_5$ | $BF_4$ | 2 | DMF[e] | 0 | 0.25 | **a** | 1.00/ – / – | 60.0 |
| 25 | $C_6H_5$ | $CF_3CO_2$ | 2 | Dioxane | 25 | 12 | **a** | 0.74/0.10/0.16 | 76.0 |

[a] All compounds gave satisfactory elemental analysis; C ± 0.06%, H ± 0.07%, N ± 0.06%. [b] Determined by $^1$H-NMR from the reaction mixture. [c] Based on mercury(II) salt. [d] The gummy reaction mixture could not be stirred. [e] In longer runs mercury(0) precipitates.

## CONCLUSIONS

Clear differences have been found in the mechanism of the oxy- and aminomercuration of olefins by means of the comparative study of the mercuration of *cis-cis*-1,5-cyclooctadiene. While the oxymercuration is a reversible process unless a base (i.e. sodium acetate) is added to the reaction media, the aminomercuration is reversible only when the mercury(II) salt derives from a strong acid. By the contrary the aminomercuration of olefins with mercury(II) acetate has been found an irreversible process which only leads to kinetically controlled products.

The methods described in this paper allow the direct transformation of *cis-cis*-1,5-COD **1** into different 9-azabicyclononanes in a selective manner in good yield. Since only multi-step approaches were previously known,[12b] the methods described herein should be the routes of choice for these compounds.

## EXPERIMENTAL

*Materials.* cis-cis-1,5-cyclooctadiene, aromatic amines and mercury(II) salts were commercially available and were used as received. Tetrahydrofuran was destilled from sodium-benzophenone or potassium under argon for runs under anhydrous conditions.

### *General methods*

Solvent extracts of reaction products were appropriately washed and dried ($Na_2SO_4$) before removal of the solvent. The following spectrometers were used: IR, PyeUnicam SP 1000 and Perkin–Elmer 577 ($\nu_{max}$ given in reciprocal centimetres); $^1$H NMR, Varian EM-390, and Varian FT-80A (chemical shifts are reported in parts per million ($\delta$) downfield from $Me_4Si$); $^{13}$C NMR, Varian FT-80A (chemical shifts are reported in parts per million ($\delta$) downfield from $Me_4Si$). GC analysis were performed with a Varian Aerograph 2800 and a Varian 6000 Vista Series equipped with a column Chromosorb G-1.5%. OV-101. For TLC and column separations silica gel (Merck) was used with toluene–hexane (4 : 5) as eluant.

*Oxymercuration of cis-cis-1,5-cyclooctadiene with mercury(II) Acetate and sodium acetate in water.* To a solution of mercury(II) acetate (3.2 g, 10 mmol), sodium acetate (0.8 g, 10 mmol) and water (6 mL), 1,5-COD (0.5 g, 5 mmol) was added, and the mixture stirred for 40 min. Afterwards, a sample of the reaction mixture was treated with 1N KOH, no yellow precipitate of HgO was obtained. The $^{13}$C NMR ($H_2O$) spectrum of the solution revealed the existence of a mixture of compounds **10** and **12** with a 0.45/0.55 isomer ratio. $^{13}$C NMR ($H_2O$) 180.53(s), 82.95(d), 73.81(d), 54.49(s), 49.96(s), 37.42(t), 36.97(t), 33.10(t), 28.39(t), 23.94(q). The mixture was stirred for additional hours and then the new isomer ratio found was 0.47/0.53.

*Oxymercuration of* cis-cis-1,5-*Cyclooctadiene with mercury(II) Acetate in water.* To a solution of mercury(II) acetate(3.2 g, 10 mmol) and water(6 mL), 1,5-COD(0.5 g, 5 mmol) was added and the mixture stirred for 30 min. Afterwards, a sample of the reaction mixture was treated with 1N KOH, no yellow precipitate of HgO was obtained. The $^{13}$C NMR ($H_2O$) spectrum of the solution revealed the existence of a mixture of compounds **10** and **12** with a 0.55/0.45 isomer ratio. $^{13}$C NMR ($H_2O$) 179.67(s), 82.95(d), 73.82(d), 54.54(s), 50.00(s), 37.42(t), 36.97(t), 33.07(t), 28.36(t), 23.43 (q). The mixture was stirred for 24 additional hours, and then, more than 95% conversion into **12** was found. $^{13}$C NMR (3N KOH) 183.87(s), 74.20(d), 48.36(s), 37.59(t), 28.06(t), 25.20(q).

*Oxymercuration of* cis-cis-1,5 *cyclooctadiene with mercury(II) Nitrate in water.* To a solution of mercury(II) nitrate (3.3 g, 10 mmol) and water (4 mL), 1,5-COD(0.5 g, 5 mmol) was added and the mixture stirred for a few seconds. A sample of the reaction mixture was immediately treated with 1N KOH; no yellow precipitate of HgO was obtained. A white precipitate appeared which was filtered, washed with methanol and dried. The $^{13}$C NMR (3N KOH) showed the presence of **12** uncontaminated from isomer **10** ($NO_3$). $^{13}$C NMR (3N KOH) 74.24(d), 48.36(s), 37.59(t), 28.06(t).

*Synthesis of 2,5-dichloromercury-N-Phenyl-9-azabicyclo[4.2.1]nonane* **7a**(*X* = *Cl*). To a solution of mercury(II) acetate(31 g, 100 mmol) and aniline (18 mL, 200 mmol) in dioxane(300 mL), 1.5-COD(12 mL, 100 mmol) was added and the mixture stirred for 24 h. A white precipitate is filtered and characterized as a mercury(I) salt by treatment with 1N NaOH. The reaction mixture was poured into a saturated KCl solution appearing a white precipitate which is filtered, washed with water and dried. Then it is dissolved in dioxane(300 mL) and successively treated with aniline (38 mL), 0.5N NaOH(300 mL), and $NaBH_4$(0.65 g, 17.5 mmol), dissolved in 2.5N NaOH(7.5 mL). Nearly quantitative mercury(0) precipitated and was filtered. The work up procedure was analogous to that described for runs listed in Table 1 to afford N-phenyl-9-azabicyclo[4.2.1]nonane.

*HCl Promoted rearrangement* **7**→**8**. To different solutions of 2,5-dichloromercury-N-phenyl-9-azabicyclo[4.2.1]nonane **7a**(X = Cl)(3.4 g, 5 mmol) in DMF(30 mL), the following amounts of 2N HCl were added respectively (a) 0.5 mL, room temperature; (b) 1 mL, room temperature; (c) 1 mL, 40°C (d) 2.5 mL, room temperature. The reaction mixtures were stirred for 48 h. The solutions were first neutralized and then, succesively treated with aniline(9 mL), 0.5N NaOH(15 mL), and $NaBH_4$(0.13 g, 3.5 mmol) dissolved in 2.5N NaOH(1.5 mL). Nearly quantitative mercury(0) precipitated and was filtered. The work up procedure was analogous to that described for runs listed in Table 1. The **4 : 5** isomer ratio found ($^1$H NMR) was: (a) 0.76/0.24, (b) 0.60/0.40, (c) 0.45/0.55, (d) 0.25/0.75.

*Aminomercuration of* cis-cis-1,5-*cyclooctadiene with mercury(II)-nitrate or mercury(II) tetrafluoroborate at room temperature.* To a solution of mercury(II) salt(10 mmol) and aniline(0.9 mL, 10 mmol) in DMF(30 mL), 1,5-COD (1.2 mL, 10 mmol) was added and the resulting mixture stirred at room temperature for 48 h. Nearly quantitative mercury(0) precipitated and was filtered. The reaction mixture was extracted with ether and the organic layer evaporated to give an oily residue which was purified by preparative column chromatography (silica gel; toluene–hexane–diethylamine 75 : 15 : 10). A major product not fully identified ($C_{26}H_{29}N_3$) was obtained. Elemental analysis: C, 81.42%; H, 7.62%, N, 10.96%.

*Alternative synthesis of 5-N-phenylaminocyclooctene* **13a**. To a pre-cooled solution of 2,6-dibromomercury-9-N-phenylazabicyclo[4.2.1]nonane (18.9 g, 25 mmol) in anhydrous THF(100 mL), Lithium powder(1 g, 150 mat-g) was added and the resulting mixture stirred under Argon at 0° for 11 h. Then, methanol(10 mL) was added dropwise and the reaction mixture was allowed to reach room temperature. Water was added and the organic layer worked up in the usual manner and evaporated. The residue was chromatographed to yield **13a**(3.1 g, 62%) and **4a**(0.3 g, 6%).

*Aminomercuration-reduction of* cis-cis-1,5-*cyclooctadiene with mercury(II) salts and aromatic amines. Runs* 1–25, *Table* 1. To a solution of the corresponding amine and mercury(II) salt (10 mmol) (in the molar ratio shown in Table I in 40 mL of the corresponding solvent, 1,5-COD (2.2 g, 20 mmol) was added and the mixture stirred at room temperature or 0° for 15 min to 48 h (see Table 1). The resulting solutions (runs 1–6 and 13–25) was then successively treated with 0.5N NaOH (30 mL), aniline(2.6 mL) and $NaBH_4$(0.3 g, 7 mmol) dissolved in 2.5N NaOH(3 mL). For mercurations in acetonitrile(runs 7-12) the solvent was previously removed under vacuum and the residue dissolved in THF(40 mL). Nearly quantitative mercury(0) precipitated and was filtered off. The reaction mixture was extracted with ether and the organic layer evaporated to give an oily residue which purified by preparative column chro-

Table 1. NMR spectral data ($\delta$ ppm, TMS) for compounds **4**, **5** and **13**

| Compound | $^1$H-NMR | $^{13}$C-NMR |
|---|---|---|
| **4a** | 1.1-2.4(m,12H), 4.2(s,2H), 6.3-7.2(m,5H) | 147.38(s), 130.78(d), 116.01(d), 112.91(d), 56.12(d), 33.38(t), 32.41(t), 25.67(t) |
| **4b** | 1.1-2.2(m,15H), 4.1(m,2H), 6.2-7.0(m,4H) | 142.97(s), 128.82(d), 122.34(s), 11o.39(d), 53.95(d), 31.60(t), 30.01(t), 23.19(t), 19.02(q) |
| **4c** | 1.1-2.2(m,12H), 4.1(m,2H), 6.1-7.0(m,4H) | 146.25(s), 128.07(d), 128.46(s), 111.41(d), 54.12(d), 31.29(t), 29.94(t), 23.05(t) |
| **4d** | 1.2-2.3(m,12H), 4.1(m,2H), 6.1-7.4(m,4H) | 148.71(s), 132.52(d), 113.47(d), 113.47(s), 55.58(d), 32.85(t), 31.51(t), 24.57(t) |
| **4e** | 1.2-2.2(m,15H), 4.2(m,2H), 6.2-7.1(m,4H) | 145.68(s), 138.69(s), 129.10(d), 115.47(d), 111.90(d), 108.55(d), 54.61(d), 32.39(t), 30.85(t), 24.03(t), 21.81(q) |
| **5a** | 1.1-2.1(m,12H), 4.0(m,2H), 6.4-7.3(m,5H) | 149.53(s), 128.60(d), 128.46(d), 113.04(d), 47.51(d), 27.78(t), 19.90(t) |
| **5b** | 1.2-2.3(m,15H), 3.9(m,2H), 6.6-7.1(m,4H) | 146.33(s), 129.78(d), 124.18(s), 112.92(d), 47.51(d), 27.33(t), 19.37(t), 17.34(q) |
| **5c** | 1.1-2.1(m,12H), 3.8(m,2H), 6.5-7.1(m,4H) | 148.63(s), 128.00(d), 127.87(s), 113.87(d) 47.66(d), 27.31(t), 19.17(t) |
| **5d** | 1.2-2.4(m,12H), 3.9(m,2H), 6.5-7.3(m,4H) | 150.40(s), 130.90(d), 114.39(d), 110.58(s), 47.61(d), 27.77(t), 19.17(t) |
| **5e** | 1.3-2.2(m,15H), 3.9(m,2H), 6.1-7.0(m,4H) | 149.20(s), 138.60(s), 129.03(d), 116.99(d), 114.33(d), 110.77(d), 48.15(d), 28.31(t) 21.63(q), 20.42(t) |
| **13a** | 1.2-2.2(m,10H), 3.3(s,1H), 3.3(m,1H) 5.3(m,2H), 6.2-7.0(m,5H) | 146.41(s), 129.29(d), 129.01(d), 128.34(d), 115.94(d), 112.50(d), 51.43(d), 34.66(t), 33.43(t), 25.79(t), 25.28(t),22.61(t) |
| **13c** | 1.1-2.3(m,10H), 3.3(s,1H), 3.3(m,1H) 5.5(m,2H), 6.1-7.0(m,4H) | 144.79(s), 129.20(d), 128.65(d), 127.98(d), 113.29(d), 51.74(d), 34.45(t), 33.11(t), 25.52(t), 25.03(t), 22.09(t) |
| **13d** | 1.3-2.2(m,10H), 3.4(s,1H), 3.4(m,1H) 5.5(m,2H), 6.0-7.1(m,4H) | 131.93(s), 130.88(d), 129.23(d), 128.76(d), 113.91(s), 51.79(d), 34.41(t), 33.07(t) 25.54(t), 25.06(t), 23.33(t) |

matography(silica gel, toluene–hexane 4:5) with the following elution order: **4**, **5**, **13**.

## REFERENCES AND NOTES

[1] For recent reviews see [a]R. C. Larock, *Angew. Chem. Int. Ed. Engl.* **17**, 27 (1978) *Tetrahedron* **38**, 1713 (1982); [b]*The Chemistry of Mercury*" Edited by J. McAuliffe MacMillan, London (1977).

[2a]W. Kitching, *Organometal. Chem. Rev.* **3** 61 (1968); [b]R. D. Bach, R. N. Brummel, and R. F. Richter, *Tetrahedron Letters*, 2879 (1971).

[3] G. A. Olah and P. R. Clifford, *J. Am. Chem. Soc.* **92**, 6967 (1970).

[4] J. J. Perie and A. Lattes, *Bull. Soc. Chim. France* 1378 (1971).

[5] J. J. Perie and A. Lattes, *Ibid* 583 (1970).

[6] R. C. Griffith, R. J. Gentile, T. A. Davidson and F. L. Scott, *J. Org. Chem.* **44**, 3580 (1979).

[7a]H. Stetter and E. F. Schwartz, *Chem. Ber.* **101**, 2464 (1968); [b]H. Stetter and E. F. Schwartz, *Chem. Ber.* **101**, 2889 (1968).

[8a]F. G. Bordwell and M. L. Douglass, *J. Am. Chem. Soc.* **88**, 993 (1966); [b]S. Moon, J. M. Takakis and B. H. Waxman, *J. Org. Chem.* **34**, 2951 (1969).

[9a]C. Ganter, K. Wiecker, W. Zwahlen and K. Schaffner-Sabba, *Helv.* **53**, 1618 (1970); [b]C. Ganter, R. O. Duthaler and W. Zwahlen, *Helv.* **54**, 578 (1971).

[10] H. C. Brown, P. J. Geoghegan, Jr., J. T. Kurek and G. J. Lynch, *Organometal. Chem. Syn.* **1**, 7 (1970–71).

[11] V. Gómez-Aranda, J. Barluenga, G. Asensio and M. Yus, *Tetrahedron Letters* 3621 (1972).

[12a]M. Barrelle and M. Apparu, *Tetrahedron Letters* 3611 (1976); [b]M. Barrelle and M. Apparu, *Tetrahedron* **33**, 1309 (1977).

[13] J. R. Wiseman and H. O. Grabbenhoft, *J. Org. Chem.* **40**, 3222 (1975).

[14] E. M. Engler, J. D. Andose and P. von R. Scheeyer, *J. Am. Chem. Soc.* **95**, 8005 (1973).

[15] The addition of two molecules of amine has not been observed even in the presence of a great excess of amine in the reaction media.

[16] In a former communication (Ref. 11), on the grounds of the results of the oxymercuration we assigned erroneously the structure **5** to compounds **4** based on the PRM spectra. See also Ref. 12*a*).

[17] H. L. Roberts, *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 11, p. 309. Academic Press, New York (1968).

[18] By analogy, it is noteworthy that transoxymercuration reactions occur much faster when the Hg–X bond in the oxymercurial is ionic (X = $ClO_4 > NO_3 > OAc \gg Cl$) while the oxymercurations are only observed with mercury halides.[19] For example see Ref. 2*b*).

[19] W. S. Linn, W. L. Waters and M. C. Caserio, *J. Am. Chem. Soc.* **92**, 4018 (1970).

[20] J. Barluenga, J. Lopez-Prado, P. Campos and G. Asensio, *Tetrahedron*, **39**, 2863 (1983).

[21] H. C. Brown and P. J. Geoghegan, Jr. *J. Org. Chem.* **35**, 1844 (1970).