

# 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

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**Abstract**—The aminomercuriation 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 oxymercuriation reactions. A selective synthesis of the title compounds is described by kinetically or thermodynamically controlled aminomercuriation of *cis-cis*-1,5-cyclooctadiene.

The mechanism and utility in organic synthesis<sup>1</sup> of oxymercuriation 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 transoxymercuriation and deoxymercuriation reactions,<sup>2</sup> and also by the spectroscopic detection of mercurinium cations.<sup>3</sup> By contrast the mechanism of the synthetically useful aminomercuriation processes has received comparatively little attention. Moreover, some results might be obscured by later rearrangements in the reduction step<sup>4</sup> and others, such as the different rate of aminomercuriation observed with the use of various mercury(II) salts have been found to be contradictory.<sup>5,6</sup> On the other hand, the question of the reversible or irreversible character of the aminomercuriation reaction has not arisen so far.

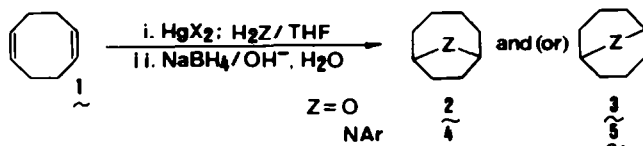
The mercuriation-demercuration reaction of *cis-cis*-1,5-cyclooctadiene **1** has been widely studied as an insight to the synthesis of 9-oxa- and 9-azabicyclononane derivatives.<sup>7-12</sup> However, the results of the reaction have been often the subject of some controversy, since the two isomeric 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 mercuriation step. In addition, the differentiation between these two types of skeletal arrangements was difficult until the introduction of <sup>13</sup>C NMR.<sup>13</sup>

It was likely that the alternative formation of these bicyclic skeletons could result from a kinetically or thermodynamically controlled mercuriation process and, hence, we felt that the study of the mercuriation 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 aminomercuriation is a reversible process.

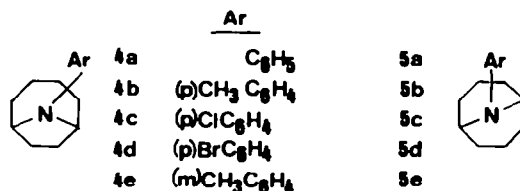
For the above reasons, we wish to report now our detailed study on the reaction of *cis-cis*-1,5-cyclooctadiene with aromatic amines in the presence of a series of mercury(II) salts by using different molar ratios and solvents which enables to clarify the question of the reversibility of the aminomercuriation of olefins. As a result, we propose a mechanism for the aminomercuriation 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<sup>14</sup> indicate that bicyclo[3.3.1]nonane is more stable than bicyclo[4.2.1]nonane by 47.57 kJ mol<sup>-1</sup>. Since the substitution of the amine nitrogen for the sp<sup>3</sup> hybridized bridge carbon should not reverse the stability order, we assume that under thermodynamic control, i.e. in a reversible aminomercuriation of *cis-cis*-1,5-cyclooctadiene **1**, the [3.3.1] isomer **8** will predominate. The cyclization reaction will proceed in two



Scheme 1.

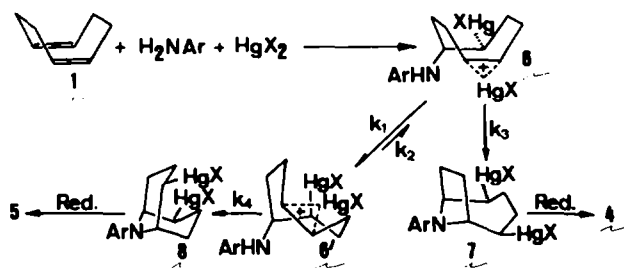


steps, the latter of them being the fast intramolecular aminomercuration of the second double bond.<sup>15</sup> For geometric reasons, the formation of the transition state which leads to the aminomercurial 7 is expected to be kinetically favourable as it does not require any conformational change and 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 (Scheme 3, Path a) which leads to 9-oxabicyclo[4.2.1]nonane 2 uncontaminated by the 1,5-epoxide isomer 3.<sup>1</sup> 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.<sup>1</sup> 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 mercuriation was complete in 40 min and a 0.55/0.45 mixture of the oxymercurials 10 and 12 was obtained (Scheme 4). When the oxymercuriation mixture was stirred for 24 additional hours the 10:12

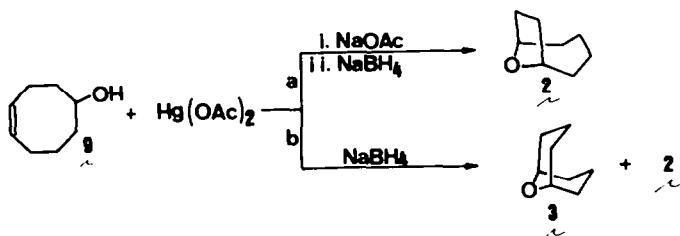
isomer ratio found was 0.47/0.53. Thus, the isomerization 10→12 is a very slow process in weak alkaline media.

The mercuriation 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 oxymercuriation mixture was allowed to stand for 24 hr at room temperature a nearly total conversion of 10 into 12 was observed (Scheme 4). The mercuriation with mercury(II) nitrate afforded 12 (as NO<sub>3</sub> derivative) as a single isomer in only a few seconds. The progress of the oxymercuriation reaction was followed in all instances by <sup>13</sup>C NMR. Reactions were considered to be complete when no yellow precipitate of mercury(II) oxide was obtained upon treatment of a sample from the reaction mixture with 1N potassium hydroxide.

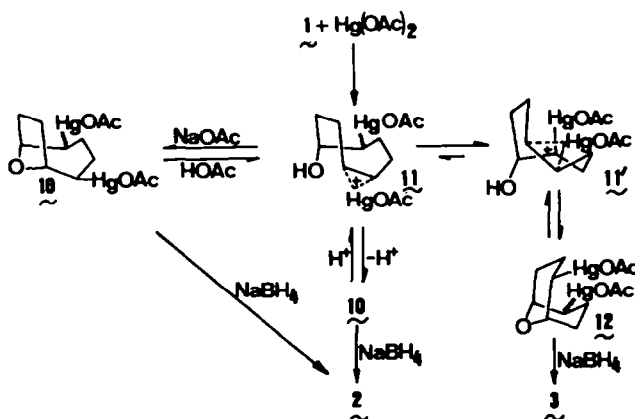
In contrast, aminomercuriation of 1 with mercury(II) acetate (Scheme 2, X = OAc) leads, independently of the reaction time or temperature, only to the 1,4-azabicycloalkane 4 and less than 10% of the 1,5-isomer 5.



Scheme 2.



Scheme 3.



Scheme 4.

The different course of oxy- and aminomercurcation reactions under similar conditions suggests that the acetic acid generated in the mercurcation, promotes the rearrangement of the kinetic oxymercurcation adduct **10** through the equilibrium between **11** and **11'** which implies the acid catalyzed deoxymercurcation of **10** (Scheme 4).

On the contrary, acetic acid fails to promote the deaminomercurcation of the adduct **7** ( $X = \text{OAc}$ ). Then, it is inferred that aminomercurcation 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<sup>16</sup> (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 mercurcation step.

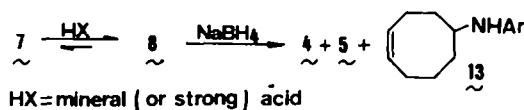
The use of mercury(II) salts of mineral acids leads after sodium borohydride reduction to 1,5-azabicyclo **5** by rearrangement of the kinetic aminomercurial **7** initially formed (see Table 1). Mercury(II) nitrate, tetrafluoroborate, trifluoroacetate, bromide and chloride were tested as mercurating 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<sup>17</sup> and the presence of a strong acid responsible for the existence of **7** in the protonated form. Since aminomercurcations were carried out in the presence of an excess of olefin, it can be deduced that the conversion **7**→**8** does not imply a transaminomercurcation but a monodeaminomercurcation reaction.<sup>18</sup>

Compounds **8** ( $X = \text{Cl}$ ) can be alternatively synthesized by rearrangement of the isolated aminomercurials **7** ( $X = \text{Cl}$ ) when these are treated with two equivalents of concentrated hydrochloric acid in DMF solution at room temperature for 48 h. Aminomercurial **7** ( $X = \text{Cl}$ ) are prepared in nearly quantitative yield by aminomercurcation 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** ( $X = \text{Cl}$ ) 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).

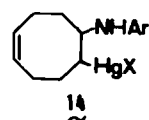
The rate of aminomercurcation increases with the ionic character of the mercury salt and the polarity of the solvent but the extent to which the rearrangement **7**→**8** takes place largely depends on the temperature and reaction time (see Table 1). For instance, with mercury(II) nitrate at temperatures 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 aminomercurcation mixture  $\delta,\gamma$ -unsaturated amines **13** (Scheme 6) were always detected and isolated in variable yield.

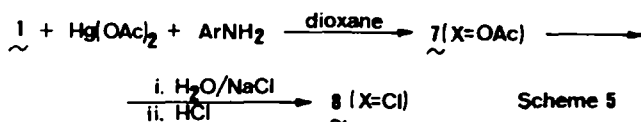


Scheme 6.

The largest unsaturated amine/bicyclic compound ratio was found in mercurcations 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 deaminomercurcation of **7** and/or **8** in the reduction step. Since the formation of **13** from isolated **7** ( $X = \text{OAc}$ ,  $\text{Ar} = \text{C}_6\text{H}_5$ ) is almost completely avoided by the use of the appropriate homogeneous reduction conditions,<sup>20</sup> it is likely that **13** ( $\text{Ar} = \text{C}_6\text{H}_5$ ) derives from the aminomercurcation process itself and not from deaminomercurcation of **8** ( $X = \text{Cl}$ ) 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.<sup>21</sup>



Scheme 5.

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

Run	ArNH <sub>2</sub> (Ar)	HgX <sub>2</sub> (X)	Amine/Hg(II) molar ratio	Solvent	Temperature °C	Reaction time h	Products <sup>a</sup> 4,5,13	Ratio <sup>b</sup> 4/5/13	Yield(%) <sup>c</sup> 4+5
1	C <sub>6</sub> H <sub>5</sub>	Cl	2	THF	25	1	a	0.28/0.53/0.19	9.5
2	C <sub>6</sub> H <sub>5</sub>	Cl	2	THF	25	6	a	0.25/0.56/0.19	28.0
3	C <sub>6</sub> H <sub>5</sub>	Cl	2	THF	25	24	a	0.21/0.63/0.16	39.0
4	C <sub>6</sub> H <sub>5</sub>	Cl	2	THF	25	48	a	0.17/0.66/0.17	42.0
5	C <sub>6</sub> H <sub>5</sub>	Cl	2	DMF	25	1	a	0.64/0.27/0.09	34.5
6	C <sub>6</sub> H <sub>5</sub>	Cl	1	THF/H <sub>2</sub> O(3:1)	25	48	a	- /1.00/ -	64.0
7	C <sub>6</sub> H <sub>5</sub>	Cl	1	CH <sub>3</sub> CN	25	48	a	- /1.00/ -	64.0
8	C <sub>6</sub> H <sub>5</sub>	Cl	1	THF(anh)	25	48	a	- /1.00/ -	20.0
9	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Cl	1	CH <sub>3</sub> CN	25	48	b	- /1.00/ -	60.0
10	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	Cl	1	CH <sub>3</sub> CN	25	48	c	- /1.00/ -	68.0
11	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	Cl	1	CH <sub>3</sub> CN	25	48	c	- /1.00/ -	51.2
12	<i>m</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Cl	1	CH <sub>3</sub> CN	25	48	d	- /1.00/ -	73.0
13	C <sub>6</sub> H <sub>5</sub>	AcO	2	THF	25	6	e	0.85/0.15/ -	36.0
14	C <sub>6</sub> H <sub>5</sub>	AcO	2	THF	25	24	e	0.85/0.15/ -	70.0
15	C <sub>6</sub> H <sub>5</sub>	AcO	2	THF	25	96	a	0.85/0.15/ -	78.0
16	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	AcO	2	THF	25	24	a	0.85/0.15/ -	80.0
17	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	AcO	2	THF	25	24	b	0.85/0.15/ -	79.0
18	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	AcO	2	THF	25	24	b	0.85/0.15/ -	78.0
19	<i>m</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	AcO	2	THF	25	24	c	0.85/0.15/ -	82.0
20	C <sub>6</sub> H <sub>5</sub>	NO <sub>3</sub>	2	THF <sup>d</sup>	25	2	e	0.76/0.19/0.05	45.0
21	C <sub>6</sub> H <sub>5</sub>	NO <sub>3</sub>	2	DMF <sup>e</sup>	25	6	a	0.60/0.40/ -	83.0
22	C <sub>6</sub> H <sub>5</sub>	Br	2	THF	25	24	a	0.31/0.55/0.14	30.0
23	C <sub>6</sub> H <sub>5</sub>	NO <sub>3</sub>	2	DMF	0	0.25	a	1.00/ - / -	50.0
24	C <sub>6</sub> H <sub>5</sub>	BF <sub>4</sub>	2	DMF	0	0.25	a	1.00/ - / -	60.0
25	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub> CO <sub>2</sub>	2	Dioxane	25	12	a	0.74/0.10/0.16	76.0

<sup>a</sup>All compounds gave satisfactory elemental analysis; C ± 0.06%, H ± 0.07%, N ± 0.06%. <sup>b</sup>Determined by <sup>1</sup>H-NMR from the reaction mixture.

<sup>c</sup>Based on mercury(II) salt. <sup>d</sup>The gummy reaction mixture could not be stirred. <sup>e</sup>In longer runs mercury(0) precipitates.

## CONCLUSIONS

Clear differences have been found in the mechanism of the oxy- and aminomercuriation of olefins by means of the comparative study of the mercuriation of *cis-cis*-1,5-cyclooctadiene. While the oxymercuriation is a reversible process unless a base (i.e. sodium acetate) is added to the reaction media, the aminomercuriation is reversible only when the mercury(II) salt derives from a strong acid. By the contrary the aminomercuriation 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,<sup>12b</sup> 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 distilled from sodium-benzophenone or potassium under argon for runs under anhydrous conditions.

## General methods

Solvent extracts of reaction products were appropriately washed and dried ( $\text{Na}_2\text{SO}_4$ ) before removal of the solvent. The following spectrometers were used: IR, PyeUnicam SP 1000 and Perkin-Elmer 577 ( $\nu_{\text{max}}$  given in reciprocal centimetres);  $^1\text{H}$  NMR, Varian EM-390, and Varian FT-80A (chemical shifts are reported in parts per million ( $\delta$ ) downfield from  $\text{Me}_4\text{Si}$ );  $^{13}\text{C}$  NMR, Varian FT-80A (chemical shifts are reported in parts per million ( $\delta$ ) downfield from  $\text{Me}_4\text{Si}$ ). 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.

**Oxymercuriation 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  $\text{HgO}$  was obtained. The  $^{13}\text{C}$  NMR ( $\text{H}_2\text{O}$ ) spectrum of the solution revealed the existence of a mixture of compounds **10** and **12** with a 0.45/0.55 isomer ratio.  $^{13}\text{C}$  NMR ( $\text{H}_2\text{O}$ ) 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.

**Oxymercuriation 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  $\text{HgO}$  was obtained. The  $^{13}\text{C}$  NMR ( $\text{H}_2\text{O}$ ) spectrum of the solution revealed the existence of a mixture of compounds **10** and **12** with a 0.55/0.45 isomer ratio.  $^{13}\text{C}$  NMR ( $\text{H}_2\text{O}$ ) 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.  $^{13}\text{C}$  NMR (3N KOH) 183.87(s), 74.20(d), 48.36(s), 37.59(t), 28.06(t), 25.20(q).

**Oxymercuriation 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  $\text{HgO}$  was obtained. A white precipitate appeared which was filtered, washed with methanol and dried. The  $^{13}\text{C}$  NMR (3N KOH) showed the presence of **12** uncontaminated from isomer **10** ( $\text{NO}_3$ ).  $^{13}\text{C}$  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  $\text{NaBH}_4$  (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, successively treated with aniline (9 mL), 0.5N NaOH (15 mL), and  $\text{NaBH}_4$  (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 ( $^1\text{H}$  NMR) was: (a) 0.76/0.24, (b) 0.60/0.40, (c) 0.45/0.55, (d) 0.25/0.75.

**Aminomercuriation 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 ( $\text{C}_{26}\text{H}_{29}\text{N}_3$ ) 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%).

**Aminomercuriation-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 1 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  $\text{NaBH}_4$  (0.3 g, 7 mmol) dissolved in 2.5N NaOH (3 mL). For mercuriations 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	$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
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), 110.39 (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.

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