Hofmann Elimination and Stevens Rearrangement with *N,N,N*-Trimethyl-3-homoadamantylammonium Hydroxide.[1] Evidence for 3-Homoadamantene

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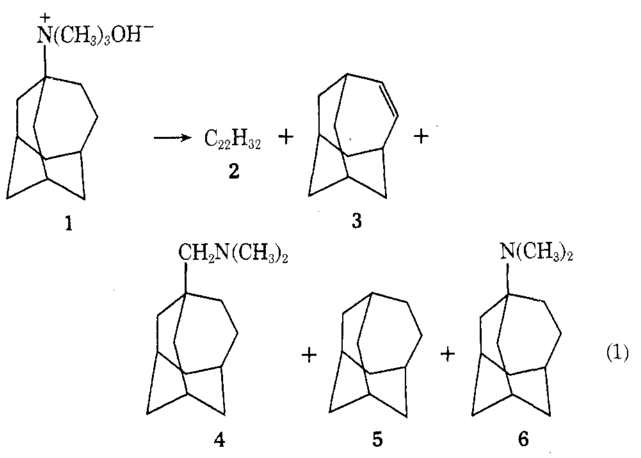
Pyrolysis of *N,N,N*-trimethyl-3-homoadamantylammonium hydroxide provided four dimers of bridgehead homoadamantene (10%), 4-homoadamantene (0.3%), *N,N*-dimethyl-3-aminomethylhomoadamantane (43%), homoadamantane (5%), and *N,N*-dimethyl-3-aminohomoadamantane (11%). The cyclobutane structure in the dimers was established by laser Raman and mass spectral data. Additional evidence for 3-homoadamantene was obtained from trapping by 1,3-diphenylisobenzofuran. *N,N*-Dimethyl-3-aminomethylhomoadamantane was formed by the unusual migration of a tertiary group during Stevens rearrangement.

Considerable interest has been shown recently in delineating the limits of Bredt's rule[4-8] and in finding a basis for predicting the degree of stability of bridgehead double bonds. Hofmann elimination[4] and bisdehalogenation of vicinal dihalides[5] have been used to produce highly strained olefins which, in many cases, have been isolated as Diels–Alder adducts or [2 + 2] dimers. Most of the prior work has been done in the bicyclic series. The isolation of dimer has been cited[5a,b] as evidence for the existence of adamantene. This report presents evidence for the formation of 3-homoadamantene as an intermediate in the pyrolysis of *N,N,N*-trimethyl-3-homoadamantylammonium hydroxide (1).

In contrast to Hofmann elimination[4] in less strained systems, a Stevens rearrangement product, arising from unusual migration of a tertiary group, was found in moderate yield. Stevens rearrangement[9] usually occurs in the absence of a β hydrogen, the presence of a rather acidic α hydrogen, or the involvement of a migrating group capable of stabilizing a negative charge or radical.

Results and Discussion

N,N,N-Trimethyl-3-homoadamantylammonium hydroxide (1) was prepared from the known amine[10] by standard techniques. Decomposition at 140–175° (1 mm) provided a mixture of dimers of 3-homoadamantene (2, 10%), 4-homoadamantene[11,12] (3, 0.3%), *N,N*-dimethyl-3-aminomethylhomoadamantane (4, 43%), homoadamantane[11] (5, 5%), and *N,N*-dimethyl-3-aminohomoadamantane[10] (6, 11%), eq 1.

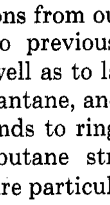


(1)

Reaction conditions are of particular importance in determining the pathway which is followed. If the procedure entails heating from room temperature, mostly parent amine is obtained. Apparently, much of the quaternary salt is destroyed by S_N2 attack[13] of hydroxide ion before rearrangement or elimination can take place.

The dimer mixture 2 was isolated as a white solid which had sublimed at the higher temperatures to cooler portions of the pyrolysis flask. Gas chromatography revealed four peaks [a (29%), b (8%), c (3%), and d (60%)]. Components **2a** and **2d** were identified as dimers of 3-homoadamantene by ir, nmr, laser Raman, and mass spectral data, elemental analysis, and comparison to dimers from Cope elimination with *N,N*-dimethyl-3-aminohomoadamantane *N*-oxide[1] and from rearrangement of 1-adamantylcarbene.[8] No report of the use of laser Raman spectroscopy for identification of this type of structure has been made prior to the communications from our[1] and Schleyer's[8] laboratories. By comparison to previous studies of substituted cyclobutanes[14,15] as well as to laser Raman spectra of homoadamantane, adamantane, and adamantene dimer,[16] we have assigned[17,18] bands to ring deformations and ring puckering in the cyclobutane structure of 2. The low-frequency Raman lines are particulary useful since similar bands were observed[14] in other systems and assigned to ring puckering.

The quaternary hydroxide 1 can eliminate to give, theoretically, two olefins, 7 and 8. These alkenes could then undergo cycloaddition resulting in a total of 16 geometric isomers. Since only four different dimers were observed by glpc analysis and three of these (**2a**, **2b**, and **2d**) correspond to dimers isolated from the rearrangement of 1-adamantylcarbene[8] which can give only 7, we conclude that decomposition of 1 proceeds essentially exclusively to 7. Alternatively, 8, if formed, rearranges quickly to 7 *via* 1,3-hydride shift.[19] Each of the isomers, **2a**, **2b**, and **2d**, gave the same glpc retention time as the corresponding dimer from 1-adamantylcarbene rearrangement,[8] and **2a** and **2d** were identical with their counterparts from 1-adamantylcarbene ac-



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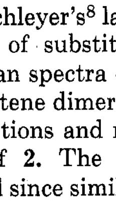

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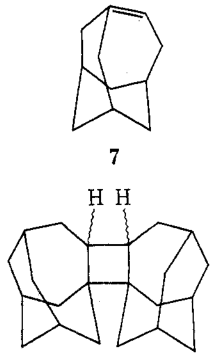
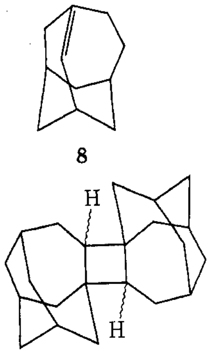


2

head-to-head (cis or trans) from 7

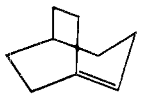


2

head-to-tail (cis or trans) from 7

cording to laser Raman spectral data. On the basis of the available spectral data, we are unable to assign definite structures to the individual dimers. However, we have tentatively suggested that major component d has the "head-to-head trans" geometry and that a is the "head-to-tail cis" isomer.[17,18,20]

The formation of olefin **3** is at variance with results[4] from the bicyclic systems, since this type of product was not observed in the earlier work. Wiseman and Chong[4c] were able to isolate bicyclo[3.2.2]non-1-ene (**9**) and bicyclo-[3.2.2]non-1(7)-ene (**10**) at Dry Ice temperatures using Hofmann elimination at the bridgehead. These olefins dimerized fairly rapidly on warming to room temperature, but did not isomerize to the more stable 2 isomer. Since **7** is more reactive than **9** and **10** and of higher molecular weight, it is not able to escape from the reaction mixture before dimerization or isomerization.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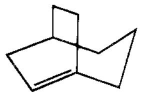
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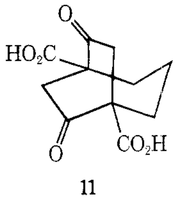
There are at least three plausible routes which could account for the presence of **3**. The intermediate bridgehead olefin **7** may undergo base-catalyzed isomerization or 1,3-hydride shift.[19] A less appealing possibility is that 1,3-elimination gives rise to 3,5-dehydrohomoadamantane, followed by 1,2-hydride shift. Since 1,3-dehydroadamantane[21] is an isolable, though reactive, compound, it is likely that some of the homoadamantyl analog would, if formed, survive the reaction conditions.

The generation of bridgehead homoadamantene **7** appears to fit Wiseman's[4a] generalization that the strain of a bridgehead double bond is closely related to the strain of the corresponding *trans*-cycloalkene. In this case the double bond is trans in a seven-membered ring and should have roughly the same amount of strain as *trans*-cycloheptene[22] and bridgehead *trans*-cycloheptenes in the bicyclic series.[4c,d] We have found no example of a strained alkene of this ring size in a tricyclic system. The additional bridge in the homoadamantyl skeleton produces a more rigid framework which would likely increase the strain of a double bond at the bridgehead. This appears to be the case with **7**.

A comparison of the keto acids **11** and **12** supports the thesis that **7** possesses somewhat greater strain than the singly bridged *trans*-cycloheptenes **9** and **10**. The mechanism[23] of decarboxylation is commonly accepted as involving an enol intermediate. Although both compounds would form a bridgehead enol trans in a seven-membered ring, **11** undergoes decarboxylation[24] at 218°, whereas **12** decomposes at a somewhat higher temperature, 280°.[25] A partial exchange of the bridgehead proton for deuterium on treatment with sodium methoxide in D_2O at reflux was found for bicyclo[4.2.1]nonan-9-one[26] (**13**). No incorporation[27] of deuterium was observed at the bridgehead of 4-homoadamantanone on exposure to sodium *tert*-butoxide–*tert*-butyl alcohol-*O-d*, even though Schleyer and coworkers[27] noted from models that the corresponding enol is not impossibly strained. Therefore, with these differences in mind, Wiseman's modification of Bredt's rule also applies in the present case.



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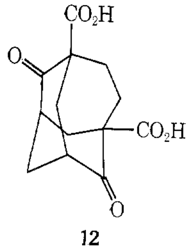

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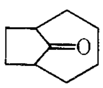

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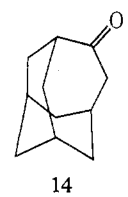

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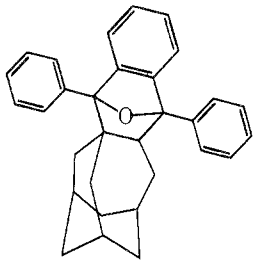
Several experiments were undertaken in order to trap the intermediate bridgehead olefin during pyrolysis. The quaternary hydroxide **1** was decomposed in the presence of 1,3-diphenylisobenzofuran (DPIBF), a reagent that has been successfully employed in previous, related work.[4,22] A 10% yield of the Diels–Alder adduct **15** was isolated from the residue in the pyrolysis flask by column chromatography on alumina, followed by purification *via* preparative thin layer chromatography on silica gel (no more than 10% of isomeric adduct could be present). Since the melting range is small, the trapped product is probably a single isomer. This evidence further supports the contention that **7** is the preferred product from elimination.



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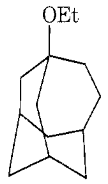
Ethanol and water were also explored as trapping agents by sealing the reactants in a glass tube which was immersed in an oil bath at 145–150° for 1–2 hr. Additions[4a,c,6,7a] of weak Brønsted acids to bridgehead olefins have been observed in bicyclic systems. Bicyclo[3.3.1]non-1-ene,[4a,6] **9**,[4c] and **10**[4c] all add acetic acid or ethanol in the presence of traces of acid. Adamantene[7a] was proposed as an intermediate in a recent study on the basis of presumed capture by methanol and methanol-*O-d*. Reaction in our case afforded the ether, 3-ethoxyhomoadamantane[28,29] (**16**, 8%), plus 3-hydroxyhomoadamantane[30] (**17**, 8%) from involvement of water present in the quaternary hydroxide or generated during reaction, in addition to **4** (62%), **5** (2%), and **6** (1%). No dimers or 4-homoadamantene (**3**) were detected in the product mixture; note that the combined yield of **16** and **17** approximates the yield of dimer from the standard system. Compound **16** was identified by ir and nmr spectra, as well as by comparison to authentic material prepared by reaction of the sodium salt of **17** with ethyl iodide. The absence of dimer **2** and olefin **3** suggests that 3-homoadamantene was successfully trapped before occurrence of dimerization or isomerization. On the other hand, **16** and **17** may arise from solvolysis. In this type of situation, one might expect some rearrangement to the thermodynamically favored[29] adamantylcarbinyl structure (alcohol **18** or ether **19**), none of which was detected. It might be that solvolyzed material exists as a tight ion–molecule pair which is not favorably disposed toward rearrangement.

Thermolysis of the quaternary deuteroxide **1**-*d* in ethanol-*O-d* did not provide straightforward corroboration of Brønsted acid addition to **7**. No C–D stretching vibration was observed in the ir spectra of **16** and **17**, and the mass



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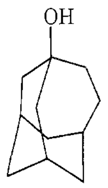

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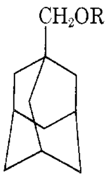
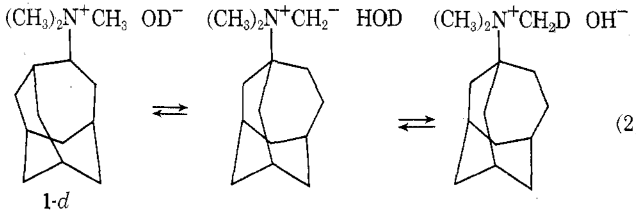


18, R = H
19, R = Et

spectrum indicated an increase of only a few per cent for the P + 1 peak. Amines **4** and **6** in the product contained 1–2 atoms of deuterium per molecule on the basis of ir and mass spectral data. A possible rationalization of the results is that proton–deuterium exchange with the methyl groups of **1**-*d*, eq 2, takes place rapidly compared to elimination, giving mostly EtOH, rather than EtOD, eq 3, in the vicinity of the forming bridgehead olefin. However, the solvolytic mechanism appears more in keeping with these observations.



1-*d*

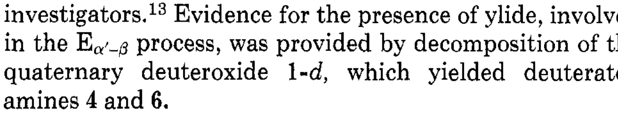
(2)

$$OH^- + EtOD \rightleftharpoons HOD + EtO^- \rightleftharpoons OD^- + EtOH \qquad (3)$$

Precise details of the elimination mechanism for quaternary salt **1** were not investigated. The impossibility of trans elimination and steric blocking of β hydrogens by the NMe_3^+ group may favor an $E_{\alpha'-\beta}$ process as stated by prior investigators.[13] Evidence for the presence of ylide, involved in the $E_{\alpha'-\beta}$ process, was provided by decomposition of the quaternary deuteroxide **1**-*d*, which yielded deuterated amines **4** and **6**.

The Stevens rearrangement product, **4**, was identified by comparison to authentic material prepared by independent synthesis. 3-Homoadamantanecarboxamide[10] was reduced with $LiAlH_4$ to give 3-aminomethylhomoadamantane. Methylation with formaldehyde and formic acid gave tertiary amine **4**, identical with the product from pyrolysis. Very little has been reported[31] on this type of rearrangement for simple tetraalkylammonium systems, with the exception of the tetramethyl type. Our results represent an unusual Stevens rearrangement, since we have found no prior examples[32] involving migration of a secondary or tertiary group.

Two mechanistic possibilities[9,33,34] have been advanced for the nature of the migrating group in this rearrangement, namely carbanion and radical. Base can remove a proton from a methyl group to give an ylide. Rearrangement then occurs by dissociation to either an ion pair, eq 4, or a radical pair, eq 5, followed by recombination. At least



$$\begin{array}{l} {}^{-}CH_2N^+(CH_3)_2 \\ \quad | \\ \quad R \end{array} \begin{array}{l} \nearrow CH_2{=}N^+(CH_3)_2 \longrightarrow RCH_2N(CH_3)_2 \qquad (4) \\ \qquad R^- \\ \searrow {}^{-}CH_2N^+(CH_3)_2 \longleftrightarrow \cdot CH_2N(CH_3)_2 \longrightarrow \\ \qquad R\cdot \qquad\qquad\qquad R\cdot \\ \qquad\qquad\qquad\qquad RCH_2N(CH_3)_2 \qquad (5) \end{array}$$

for certain systems, the radical pathway appears to be favored currently.[32,34] Migration of the homoadamantyl group is in keeping with a radical mechanism, although relief of strain may play an important role. A significant amount of crowding appears to be present in **1** owing to the two adjacent quaternary atoms (bridgehead carbon and nitrogen). It is pertinent that the analogous 1-*tert*-butyladamantane[35] has been made only with great difficulty. Pine and coworkers[33] found that the similar rearrangement in the neopentyl system was greatly influenced by steric requirements.

Formation of **4** resembles the generation of neopentane as a by-product in the Stevens rearrangement of *N,N,N*-trimethylneopentylammonium iodide.[33] Apparently the reactive intermediates can separate to some extent with subsequent abstraction of a proton[33] or hydrogen atom. Although bishomoadamantyl, theoretically possible *via* combination of the radical intermediates, was not detected, this finding does not rule out the homolytic mechanism, since the intermediates may be present in such low concentration that dimerization cannot compete with hydrogen abstraction.

In contrast to the present results, pyrolysis[4] of the bridgehead trimethylbicyclononyl and bicyclooctylammonium hydroxides afforded only the corresponding strained olefin, or its dimer, and the parent amine. No Stevens rearrangement product, isomerized olefin, or parent hydrocarbon was reported. These differences may be rationalized by the apparently greater ease of elimination in the bicyclic systems.

A comparison of the results from the adamantyl[32] and homoadamantyl systems gives an indication of the relative strain of adamantene and 3-homoadamantene and also shows the limitation of the Hofmann elimination method for producing strained olefins. In the decomposition of **1**, elimination and rearrangement occur at competing rates. For the adamantyl system, however, elimination is so unfavorable that Stevens rearrangement and S_N2 attack by hydroxide ion account for all observed products. Therefore, 3-homoadamantene would appear to be nearing the limit of the type of *trans*-cycloalkene which can be formed by Hofmann elimination.

Experimental Section

Ir spectra were obtained with a Perkin-Elmer 137 spectrophotometer (calibrated with the 1601.8-cm-$^{-1}$ band of polystyrene). Varian T-60 and HA-100 instruments were used to obtain nmr data, which are reported in parts per million (δ) (in CCl_4) relative to tetramethylsilane as internal standard. Laser Raman spectra were obtained from a Ramex Spex 1401 spectrophotometer, measured from the green excitation line (19,436 cm^{-1}). Microanalyses were performed by Baron Consulting Co., Orange, Conn., and Dr. R. E. White. Some of the mass spectral data were provided by Drs. Michael Kurz and Robert D. Fisher. Glpc analyses were conducted on Varian Aerograph 1800, 1700, and 90P instruments with the indicated columns: (I) 15% Carbowax 20M on Chromosorb W (45/60 mesh), 10 ft × 0.25 in., copper; (II) 15% Carbowax 20M and 5% NaOH on Chromosorb P (30/60 mesh), 10 ft × 0.25 in., copper; (III) 15% Carbowax 20M on Chromosorb W (45/60 mesh), 6 ft × 0.25 in., copper; (IV) 5% Carbowax 20M on Chromosorb W (45/60 mesh), 5 ft × 0.25 in., copper. Melting points (uncorrected) were obtained with a Thomas-Hoover capillary melting point apparatus.

***N,N,N*-Trimethyl-3-homoadamantylammonium Iodide.** Methyl iodide (5.9 g, 0.042 mol) was added to *N,N*-dimethyl-3-aminohomoadamantane[10] (**6**, 4 g, 0.021 mol) in 50 ml of absolute ether. A white precipitate formed immediately. After the mixture was allowed to stand overnight, the salt was filtered and dried. Recrystallization from ethanol–ether gave 4.6 g (66% yield), mp 282–283° dec.

Anal. Calcd for $C_{14}H_{26}NI$: C, 50.15; H, 7.82. Found: C, 50.02; H, 7.55.

***N,N,N*-Trimethyl-3-homoadamantylammonium Hydroxide (1).** Silver oxide (5.6 g , 0.024 mol) was added to a mixture of the ammonium iodide (5.6 g, 0.017 mol), 30 ml of distilled water, and 40 ml of ethanol. The mixture was stirred for 5 hr at room temperature and then was filtered to remove silver salts. Evaporation of solvent and drying under vacuum overnight gave 4.4 g (3.8 g, theory) of a gray-white solid which was extremely hygroscopic. Elemental analysis indicated that the crude material was approximately 74% **1**.

Pyrolysis of 1. In a typical run, 1.42 g (0.0045 mol) of **1** was placed in a 15-ml, round-bottomed flask connected through a short-path distillation head to a 10-ml receiver cooled in an acetone–Dry Ice bath. Vacuum (1 mm) was applied while the oil bath was preheated to 140°. The pyrolysis flask was immersed in the bath and heating was continued to 180° over a period of 1.5 hr. The distillate (0.86 g) was taken up in ether and extracted with 2 *N* HCl. The ether layer was dried and evaporated to give neutral products (0.11 g). Glpc analysis on column I indicated that the neutral fraction was 35% **5**,[11] mp 257–258° (sealed tube) (5.4% yield), 2% **3**,[11,12] mp 237–238° (sealed tube) (0.3% yield), and some dimeric material (<1%).

The acid layer was evaporated to approximately 1 ml and added to 50 ml of 20% NaOH. The mixture was extracted with ether. The ether solution was dried and evaporated to give 0.68 g of basic products. Glpc analysis on column II indicated 60% of **4** (43% yield) and 14% of **6**[10] (11% yield).

A white solid (0.067 g) sublimed at 180° under vacuum from the reaction mixture into the distillation head. Glpc analysis on column IV showed it to be a mixture of four components, **2a** (29%), **2b** (8%), **2c** (3%), and **2d** (60%).

Samples of **2a** and **2d** for spectra and microanalysis were collected from column III. Separation was effected on a 6-ft OV-1 column attached to a mass spectrometer.

2a: mp 252–256°; nmr δ 1.3–2.8 (broad m); ir (KBr) 2820, 2600 (w), 1445, 928, 810 (w), 785 cm^{-1} (w); mass spectrum, parent ion, *m/e* 296.

Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.89; H, 10.78.

2b: mass spectrum, parent ion, *m/e* 296.

2c: mass spectrum, parent ion, *m/e* 296.

2d: mp 195–200°; nmr δ 1.3–2.8 (broad m); ir (KBr) 2810, 2610 (w), 1440, 930, 802 (w), 783 cm^{-1} (w); mass spectrum, parent ion, *m/e* 296.

Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.91; H, 10.81.

3-Aminomethylhomoadamantane.[10] $LiAlH_4$ (1.5 g, 0.039 mol) was suspended in 40 ml of dry tetrahydrofuran. After 3-homoadamantanecarboxamide[10] (2 g, 0.011 mol) in 20 ml of dry tetrahydrofuran was added slowly, the mixture was refluxed for 72 hr and then was cooled. Water (1.5 ml), 10% NaOH (1.5 ml), and water (3 ml) were carefully added. The mixture was filtered and the precipitate was washed with ether. The combined ether layer was dried and evaporated to give crude amine (1.7 g).

***N,N*-Dimethyl-3-aminomethylhomoadamantane (4).** The crude 3-aminomethylhomoadamantane from above (1.7 g) was added to 97% formic acid (10 ml) and formaldehyde (10 g). The solution was heated at 95° for 7 hr and then was cooled. After 10 ml of 4 *N* HCl was added, the solution was evaporated to approximately 5 ml. The concentrated solution was added to 60 ml of ice-cold, 20% NaOH and the mixture was extracted with ether. The ether solution was dried and evaporated to give a reasonably pure (95%) sample of **4** (0.95 g). Glpc collection on column II provided pure **4:** ir (neat) 1430, 1250, 1140, 1027, and 835 cm^{-1}; nmr δ 2.23 (d, 8 H), 2.1–1.3 (m, 17 H).

Anal. Calcd for $C_{14}H_{25}N$: C, 81.09; H, 12.15; N, 6.76. Found: C, 81.22; H, 12.26; N, 6.59.

Homoadamantane (5). 4-Homoadamantene[11,12] (**3**, 57 mg) and Pd/C (22 mg) were added to 8 ml of absolute ethanol in a Parr apparatus. After the mixture was shaken with hydrogen for 20 hr, the catalyst was filtered and the filtrate was evaporated to give **5** (19 mg). Glpc collection on column I provided a pure sample for comparison to the corresponding product from pyrolysis.

Pyrolysis of 1 with 1,3-Diphenylisobenzofuran (DPIBF). The quaternary hydroxide **1** (2 g, 6.7 mmol) and DPIBF (2 g, 9.3 mmol) were placed in a 25-ml, round-bottomed flask connected through a short-path distillation head to a 10-ml receiver cooled in an acetone–Dry Ice bath. Vacuum (15 mm) was applied and the flask was immersed in an oil bath at 140° for 1.5 hr. At this time the vacuum was adjusted to 0.2 mm in order to remove any volatile products present in the reaction flask. After the apparatus had cooled, the residue in the pyrolysis flask was taken up in 100 ml of benzene. Maleic anhydride was added to decompose excess DPIBF. After 50% NaOH in an equal volume of methanol (25 ml) was added to the benzene, the mixture was refluxed for 30 min. The organic layer was separated, washed with water, dried, and evaporated to yield 0.83 g of yellow solid. Column chromatography on alumina (10 cm, elution with benzene) yielded 0.41 g of a yellow solid in the third fraction (25 ml). This material contained four impurities comprising about 20% of the mixture. Preparative-scale tlc with silica gel–benzene, followed by washing with ether, provided pure **15** (10% yield):[36] mp 187–190°; ir (KBr) 3000, 2895, 1595, 1490, 1445, 995, 785, 748, 701 cm^{-1}; nmr[37] δ 6.95–7.80 (m, 14 H), 1.0–2.8 (m, 16 H); mass spectrum, parent ion, *m/e* 418.

Decomposition of 1 in Ethanol. A homogeneous solution of the vacuum-dried quaternary hydroxide [0.089 g consisting of 0.068 g (3 mmol) of **1** and 0.021 g (1.2 mmol) of H_2O] in 0.27 g (5.7 mmol) of absolute ethanol was heated in a sealed tube for 2 hr at 140–145°. The resultant solution was taken up in ether, followed by extraction with 1 *N* HCl. Analysis of the ether layer for neutral products by glpc on column I indicated the presence of **5** (1.6%), **16** (7.5%), and **17** (7.8%).

After the aqueous acid fraction was added to 25% NaOH, extraction was effected with ether. The ether layer was dried and analyzed by glpc on column II. Basic products **4** (62%) and **6** (1.2%) were identified.

The product distribution was found to be sensitive to the amount of water present, with increased quantities providing substantially more **17** and **6.**

3-Ethoxyhomoadamantane[28,29] **(16).** Sodium (0.30 g, 13 mmol) was added to 3-hydroxyhomoadamantane[30] (**17**, 2.0 g, 12 mmol) in 25 ml of tetrahydrofuran. The mixture was refluxed until all of the sodium had reacted, and a fine, white powder (alkoxide) was present. After ethyl iodide (3.5 g, 0.024 mol) was added, the mixture was refluxed overnight. Glpc analysis on column I indicated a 10% yield of **16:** ir (neat) 2900, 1440, 1375, 1150, 1105, 1070, 1015, and 977 cm^{-1}; nmr δ 3.39 (q, J = 7 Hz, 2 H), 2.1–1.4 (m, 17 H), 1.04 (t, J = 7 Hz, 3 H).

***N,N,N*-Trimethyl-3-homoadamantylammonium Deuterioxide.** The deuterioxide (**1**-*d*) was prepared as described for **1**, by use of ethanol-*O*-*d* and D_2O in place of ethanol and water.

Pyrolysis of 1-*d* in Ethanol-*O*-*d*. Reaction was carried out as described for nondeuterated material. The ir spectra of **16**-*d* and **17**-*d* showed no absorption in the region of 1900–2200 cm^{-1}. The mass spectral parent peaks occurred at *m/e* 167 and 195 for **16**-*d* and **17**-*d*, with increases in P + 1 peaks of 1.7 and 1.3%, respectively.

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Registry No.—**1**, 50782-20-2; **2**, head-to-head cis, 50782-17-7; **2**, head-to-head trans, 50898-71-0; **2**, head-to-tail cis, 52208-36-3; **2**, head-to-tail trans, 50898-72-1; **3**, 24669-57-6; **4**, 50782-21-3; **5**, 281-46-9; **6**, 50782-22-4; **15**, 52175-61-8; **16**, 14504-82-6; **17**, 14504-80-4; *N,N,N*-trimethyl-3-homoadamantylammonium iodide, 52175-62-9; 3-aminomethylhomoadamantane, 52175-63-0.

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Rearrangement of *o*-Hydroxy Aldehydes and Ketones to *o*-Hydroxy Anilides by Monochloroamine[1]

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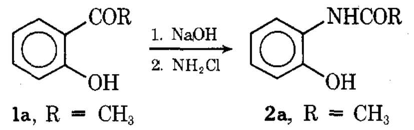
o-Hydroxy aldehydes and ketones are converted in good yield to *o*-hydroxy anilides by reaction with monochloroamine in base. The reaction was carried out with benzene nuclei containing alkyl, methoxyl, chlorine, and nitro substituents, as well as with the naphthalene nucleus. The overall transformation is similar to the Beckmann, Schmidt, Theilacker, and Pearson rearrangements. There appears to be mechanistic similarity to the Dakin oxidation.

The literature contains a number of rearrangement techniques for conversion of aromatic aldehydes and ketones to the corresponding anilides, including those of Beckmann,[3] Schmidt,[4] Theilacker,[5] and Pearson.[6] Each of these is characterized by certain limitations.

We have found a new method for the preparation of *o*-hydroxy anilides involving reaction of monochloroamine with variously substituted *o*-hydroxy aldehydes and ketones. This simple, one-step rearrangement, which takes place under mild conditions, comprises the preferred route for certain anilides. The mechanistic aspects were also investigated.

Results and Discussion

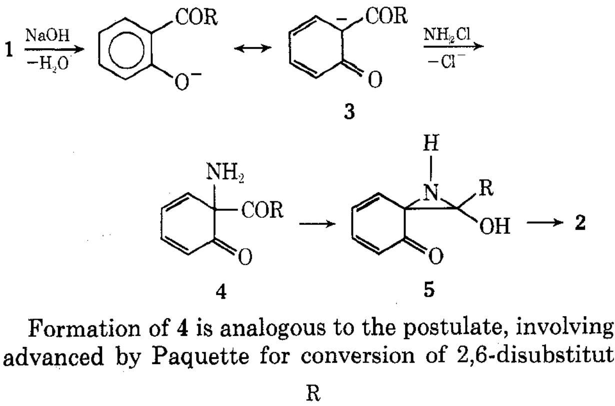
2-Acetamidophenol (**2a**) was obtained in essentially quantitative yield from addition of a caustic solution containing *o*-hydroxyacetophenone (**1a**) to aqueous monochloroamine at about 0°. The infrared spectrum of **2a** corresponded to that of authentic material. 2-Formamidophenol (**2b**), which displayed characteristic infrared absorption bands for the amide moiety, was obtained in similar manner in excellent yield from salicylaldehyde (**1b**). The melting points corresponded to the reported values. The structural assignments are also in agreement with the nmr spectra.



(1)

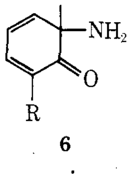
1a, R = CH_3 **2a**, R = CH_3
b, R = H **b**, R = H

The reaction pathway, eq 2, conceivably involves nucleophilic displacement of chloride ion from monochloroamine by the cyclohexadienone (phenoxide) anion (**3**) to produce amino ketone **4**. Intermediate **4** is then converted to aziridine **5**, which undergoes rearrangement to anilide **2**.



(2)

Formation of **4** is analogous to the postulate, involving **6**, advanced by Paquette for conversion of 2,6-disubstituted



6

phenoxides into dihydroazepinones *via* ring expansion by exposure to monochloroamine.[7] Kornblum and coworkers noted that the extent of C-alkylation of phenoxides increased in hydroxylic solvent.[8]

An aziridine intermediate has also been invoked in the conversion of *N*,*N*-dichloroamines to α-amino ketones.[9] Monochloroamine has been used[10] for amination of malonic esters, perhaps *via* a route analogous to the transformation of **3** to **4**.

A factor weighing against involvement of dienone **4** is the difficulty of forming this type of species, according to the prior literature. Thus, it is reported[11a] that reaction of **7**