D_2O exchangeable, NH), 3.61 (4 H, s, CH_2NCH_2), 3.83 (4 H, s, CH_2NCH_2), 7.13–7.50 (8 H, m, C_6H_4, C_6H_4).

Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.9; H, 8.0; N, 11.1. Found: C, 80.9; H, 8.2; N, 11.1.

Registry No.—**5a**, 20072-33-7; **5b**, 20072-34-8; **5c**, 20072-35-9; **5d**, 4725-83-1; **5e**, 20072-37-1; **6a**, 20072-38-2; **6b**, 20072-39-3; **7a**, 20072-40-6; **7** hydrochloride, 20072-41-7; **8a**, 20072-42-8; **9**, 20072-43-9; **10**, 20072-44-0; **10**, dihydrochloride, 20072-45-1; **11**, 20072-46-2; **12a**, 20072-47-3; **12b**, 20072-48-4; **13a** 20126-04-9; **13b**, 20072-49-5; **14**, 20072-50-8; **14**, dihydrochloride, 20072-51-9; **15**, 20072-52-0; **16**, 20072-53-1; **16** hydrochloride, 20072-54-2; **17**, 13152-91-5; **18**, hydrobromide, 20126-05-0; **19**, 20072-56-4; **20**, 20126-06-1; **21**, 20072-57-5; **21** hydrochloride, 20072-58-6; **22**, 20072-59-7; **23**, 20072-60-0.

Acknowledgment.—The authors thank Messrs. Urs Stoeckli and Alvin Schneider for instrumental and synthetic assistance.

A Novel N-CH_2-N Bridging Reaction[1a]

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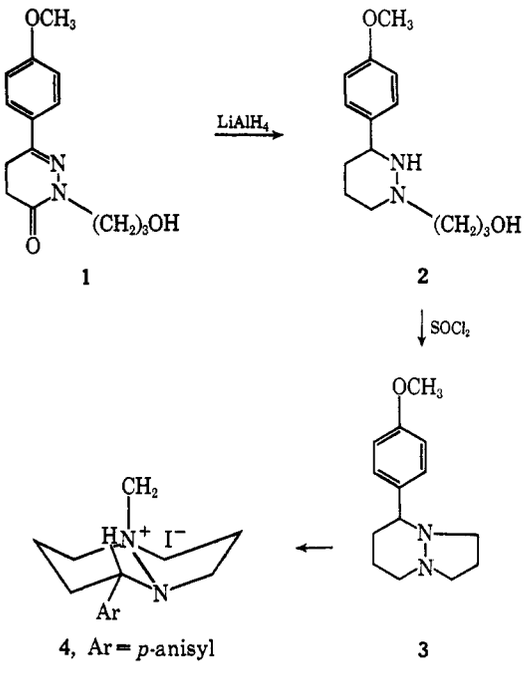
Received December 30, 1968

Treatment of the methyl iodide salts (**4** and **10**) of the bridgehead hydrazines, 2-*p*-anisyl-1,6-diazabicyclo[4.3.0]nonane (**3**) and 2-*p*-anisyl-1,6-diazabicyclo[4.4.0]decane (**9**), with refluxing sodium methoxide–methanol resulted in the formation of the N-CH_2-N bridged derivatives 2-*p*-anisyl-1,6-diaza[4.3.1]decane (**12**) and 2-*p*-anisyl-1,6-diaza[4.4.1]undecane (**14**). The same hydrazine salts when treated with sodium–ammonia gave the medium-sized ring compounds 6-*p*-anisyl-1-methyl-1,5-diazacyclononane (**13**) and 5-*p*-anisyl-1-methyl-1,6-diazacyclodecane (**15**). The formation of the NCH_2N derivatives is postulated to occur by a 1,2 shift (**17**) analogous to a Stevens rearrangement.

In the preceding paper[2] from our laboratories it was reported that the 2,6-benzodiazonine and dibenzo[*c*,*h*]-[1,6]diazecine ring systems could be prepared by the base elimination of the appropriate bridgehead hydrazine quaternary salts from 2,3,5,10-tetrahydro-1H-pyrazolo[1,2-*b*]phthalazine and 5,7,12,14-tetrahydrophthalazino[2,3-*b*]phthalazine. The present work reports our findings in the attempt to extend the synthetic usefulness of this reaction to the preparation of 1,5-diazacyclononane and 1,6-diazacyclodecane ring systems from the appropriate bridgehead hydrazine quaternary salts.

The synthesis of the required bridgehead hydrazine intermediates **3** and **9** are given in Schemes I and II. When **3** was allowed to react with methyl iodide it gave a sharp melting quaternary salt in nearly quantitative yield. The nmr of this compound gave a single methyl signal (δ 3.62) indicating that the methylation had occurred stereoselectively. Recent findings on the quaternization of piperidine[3a] and other cyclic nitrogen derivatives[3b] have shown that the methylation of these systems occurs stereoselectively with the incoming methyl group occupying an axial position. By analogy with this work we have assigned structure **4**, with an axial methyl group and an equatorial anisyl group, as the most probable conformational form.[4] Additional support for the methyl assignments will be given below.

SCHEME I



1 **2** **3** **4**, Ar = *p*-anisyl

When the mixed anhydride from 3-*p*-anisylpropionic acid (**5**) and ethyl chloroformate was allowed to react with hexahydropyridazine it gave a hydrazide that could be represented by **6** or its ring tautomer (**6a**). The ir of this compound gave carbonyl bands at 5.97 and 6.10 μ and a uv maximum at 228 mμ indicating that the tautomeric form **6** predominates. Treatment of a toluene solution of **6** with acid gave the unsaturated lactam **7**. The position of the double bond was determined from uv and nmr data. Catalytic hydrogenation of **7** afforded **8** which on further reduction with lithium aluminum hydride gave **9**. Reaction of **9** with methyl iodide gave a quaternary salt that gave a nmr spectrum with a single methyl signal (δ 3.62). By ar-

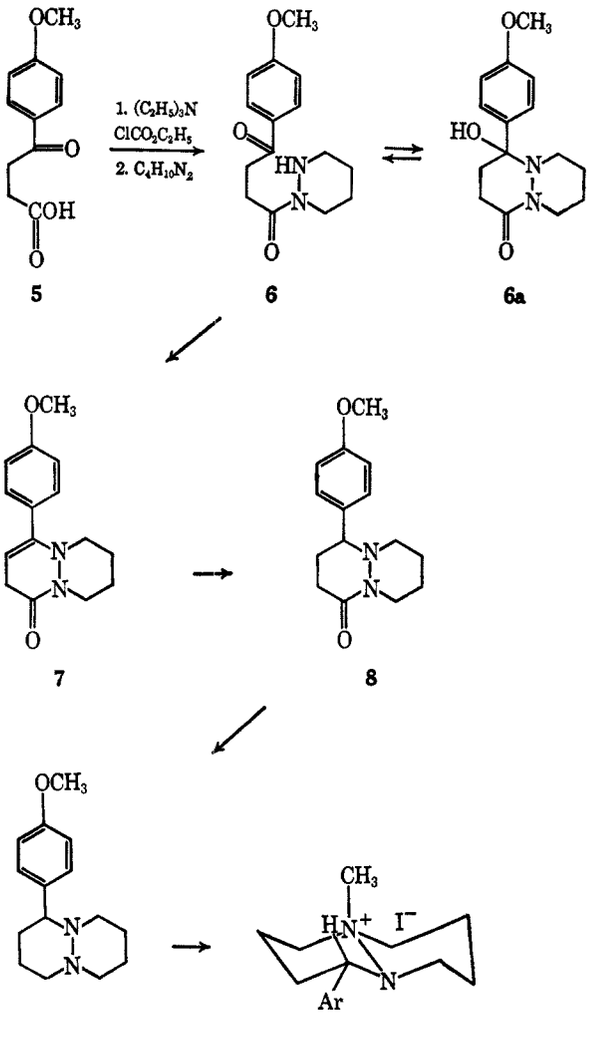
(1) (a) Portions of this paper were presented by W. J. Houlihan and R. E. Manning at the First International Congress of Heterocyclic Chemistry, The University of New Mexico, Albuquerque, N. M., June 1967. (b) Sandoz Ltd., Basel, Switzerland. (c) To whom inquiries should be sent.

(2) P. Aeberli and W. J. Houlihan, *J. Org. Chem.*, **34**, 2715 (1969).

(3) (a) Y. Kawazoe and M. Tsuda, *Chem. Pharm. Bull. Tokyo*, **15**, 1405 (1967); D. K. Brown, J. McKenna, J. M. McKenna, J. M. Stuart, and B. G. Hutley, *Chem. Commun.*, 380 (1967); H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, **31**, 1073 (1966). (b) H. O. House and C. G. Pitt, *ibid.*, 31, 1062 (1966); H. O. House and B. Terfertiller, *ibid.*, **31**, 1068 (1966); C. D. Johnson, R. A. Y. Jones, A. R. Katritzky, C. R. Palmer, K. Schofield, and R. J. Wells, *J. Chem. Soc.*, 6797 (1965).

(4) We have presumed that the indicated chair conformations (transfused) predominate in all compounds containing a six-membered ring since inspection of models reveals no apparent reason why the usual order of stability (chair > boat) should be reversed.

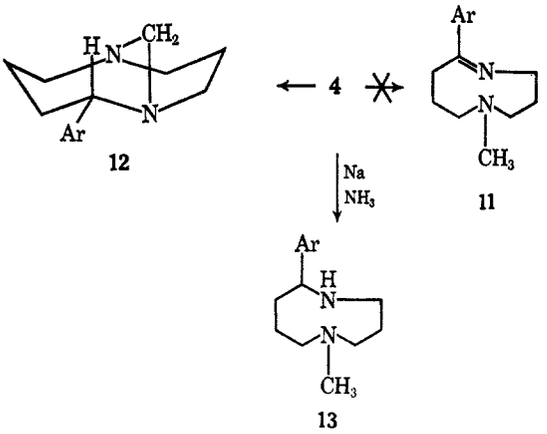
SCHEME II



guments analogous with the assignment of structure **4** we propose formula **10** for this compound.

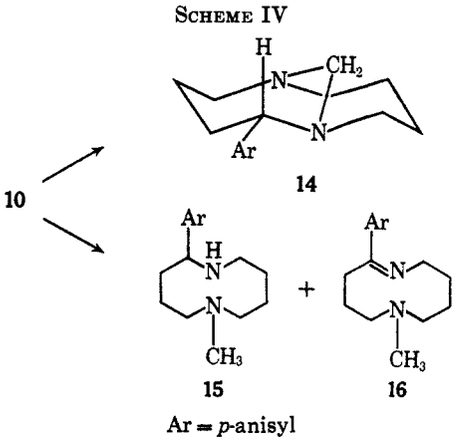
Treatment of **4** with a refluxing sodium methoxide–methanol solution gave a novel $C_{15}H_{22}N_2O$ compound. The uv spectrum of this substance gave only isolated anisyl absorption thereby ruling out structure **11**, the compound expected to be formed by analogy with the examples given in the preceding paper.[2] The nmr spectrum gave a broad 2 H singlet at δ 4.12 in addition to a OCH_3 singlet (δ 3.72) and 13 aliphatic and 4 aromatic protons. The low-field position and absence of splitting for the 2 H signal at 4.12 suggests a CH_2 grouping attached to two polar atoms that are devoid of H. Such an arrangement is present in the 1,6-diazabicyclo[4.3.1]decane structure **12** with the NCH_2N group[5] being assigned to the δ 4.12 singlet. When **4** was treated with a sodium–ammonia reducing system under conditions used to cleave $\geq C-\overset{+}{N}\leq$ bonds there resulted a $\geq N-\overset{+}{N}\leq$ cleavage to form the desired 1,5-diazacyclononane **13**. Alternative structures where a $CH_2{}^+N\leq$ cleavage occurred were ruled out since the nmr spectrum of **13** did not contain any CH_3C group. (See Scheme III.)

SCHEME III

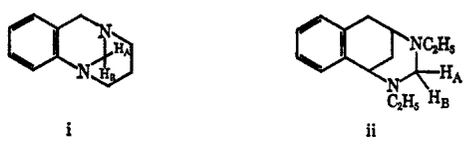


The treatment of **10** with refluxing sodium methoxide–methanol resulted in a $C_{16}H_{24}N_2O$ compound that gave isolated anisyl absorption in the uv region and an nmr spectrum with a 2 H AB pattern at δ 4.08 (H_A) and 4.42 (H_B, J = 15.0 cps), attributed to an NCH_2N group,[5] a OCH_3 singlet, 15 aliphatic and 4 aromatic protons. These data are in agreement with the 1,6-diazabicyclo[4.4.1]decane **14**. Treatment of **10** with the sodium–ammonia reducing system gave two novel compounds. The major product gave ir and nmr data consistent with the $N-N^+$ cleavage product **15**. The ir spectrum of the minor component gave a C=N bond at 6.05 μ, uv maxima at 226, 276 and 283 mμ, and nmr signals corresponding to an NCH_3 singlet (δ 2.27), 17 aliphatic and 4 aromatic protons. This compound has been assigned as the Hofmann elimination[6] product **16**. Further evidence for this structure was obtained by catalytic reduction to **15**. (See Scheme IV.)

SCHEME IV

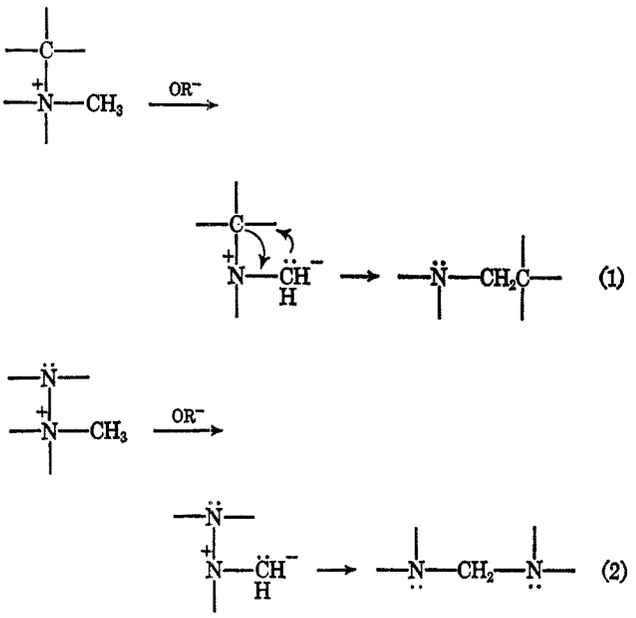


(5) The nmr signal of the NCH_2N grouping in the ring system i and ii is reported to occur as AB quartets at 3.95 (H_A), 4.26 (H_B, J = 13 cps) and 3.30 (H_A), 3.85 (H_B, J = 10.5 cps), respectively: S. Shiotani and K. Mitsuhashi, *J. Pharm. Chem. Jap.*, **14**, 608 (1966).

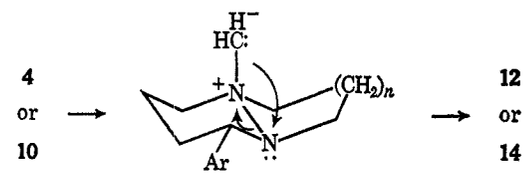


(6) The formation of Hofmann elimination products from –C—N$^+$ systems under sodium–ammonia reducing conditions has been reported: A. C. Cope, *Org. Reactions*, **11**, Chapter 5 (1960).

The formation of **12** and **14** from **4** and **10** represents a 1,2 shift analogous to the Stevens rearrangement[7] where an NN$^+$C system rather than an CN$^+$C system is undergoing rearrangement. In simplified form these transformations may be represented by eq 1 and 2.

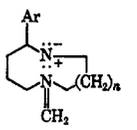


The formation of Stevens rearrangement rather than Hofmann elimination[8] products from **4** and **10** is probably due to the unfavorable steric conditions for β-H elimination. Inspection of models of **4** and **10** reveal that attack of methoxide ion on the axial benzyl hydrogen is sterically unfavorable owing to crowding of this site by the axial N$^+$CH$_3$ group. The H atoms on the N$^+$CH$_3$ group are readily accessible to methoxide ion to form the anion **17** which has the proper geometrical orientation to undergo a 1,2 shift to **12** or **14**.



17, Ar = *p*-anisyl
n = 1, 2

(7) The Stevens rearrangement has been postulated to occur by (a) an ion-pair mechanism [R. A. W. Johnstone and T. S. Stevens, *J. Chem. Soc.*, 4487 (1955); E. F. Jenny and A. Melzer, *Tetrahedron Lett.*, 3507 (1966)], (b) a stepwise internal nucleophilic displacement mechanism [C. R. Hauser and S. W. Cantor, *J. Amer. Chem. Soc.*, **73**, 1437 (1951)] that has recently been proposed to involve (c) a concerted cyclic process [H. E. Zimmerman in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, pp 378–391; E. Grovenstein, Jr., and G. Wentworth, *J. Amer. Chem. Soc.*, **89**, 1852, (1967)] and (d) carbene pathway [A. G. Anderson and M. T. Wills, *J. Org. Chem.*, **33**, 537 (1968)]. The pathway given in eq 2 corresponds to the stepwise nucleophilic displacement (eq 1). We do not consider that this is the only possible pathway for forming **12** and **14**. Ion-pair intermediates such as iii are also possible.



iii, n = 1,2
Ar = *p*-anisyl

(8) For a recent discussion on the Hofmann elimination in cyclic hydrocarbons, see M. P. Cooke, Jr., and J. L. Coke, *J. Amer. Chem. Soc.*, **90**, 5556 (1968).

Experimental Section[9]

4-*p*-Anisyl-2-(3-hydroxypropyl)-5,6-dihydropyridazin-1(2H)-one (1).—A mixture of 20.8 g (0.10 mol) of 3-*p*-anisoylpropionic acid, 13.5 g (0.15 mol) of 3-hydrazinopropanol,[10] and 250 ml of toluene was stirred and refluxed in a flask equipped with a Dean–Stark tube until the "water" level in the side arm remained constant. The solvent was removed *in vacuo* and the residue gave 21 g (81%) of **1**: mp 117–118°; ir (KBr) 6.05 μ (C=O).

Anal. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.1; H, 6.9; N, 10.7. Found: C, 64.0; H, 6.7; N, 10.6.

3-*p*-Anisyl-1-(3-hydroxypropyl)hexahydropyridazine (2).—A slurry of 14.3 g (0.376 mol) of lithium aluminum hydride and 1500 ml of diethyl ether (nitrogen atmosphere) was stirred and refluxed (72 hr) through a Soxhlet apparatus containing 50.0 g (0.19 mol) of **1**. After cooling in an ice bath the reactants were treated with 28.6 ml of 2 *N* sodium hydroxide, 42.9 ml of water, and 50 g of anhydrous sodium sulfate. The salts were filtered off and the filtrate was concentrated *in vacuo* to give 46 g of **2** as an oil: nmr ($CDCl_3$) δ 1.87 (6 H, m, CH_2CH_2, CH_2), 2.28–3.24 (4 H, m, CH_2NCH_2), 3.63 (2 H, t, J = 6.0 cps, CH_2OH), 3.73 (3 H, s, OCH_3), 3.82 (2 H, D_2O exchangeable, NH, OH), 3.88 (1 H, m, ArCHN), 7.10 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.2; H, 8.8. Found: C, 67.4, H, 8.7.

2-*p*-Anisyl-1,6-diazabicyclo[4.3.0]nonane (3).—A mixture containing 50.0 g (0.20 mol) of **2**, 35.7 g (0.30 mol) of thionyl chloride, and 500 ml of dry chloroform was refluxed for 18 hr. The solution was washed with 100 ml of 2 *N* $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 47.5 g of oil. Distillation gave 33.2 g (72%) of **3**: bp 150–152° (2.0 mm); n^{20}D 1.5507; nmr ($CDCl_3$) δ 1.52–3.40 (13 H, series of overlapping multiplets), 3.78 (3 H, s, OCH_3), 7.08 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.4; H, 8.6. Found: C, 72.7; H, 8.5.

A solution of **3** in diethyl ether was treated with anhydrous HCl to give the hydrochloride of **3**, mp 135–138° (hygroscopic).

Anal. Calcd for $C_{14}H_{21}ClN_2O$: C, 62.6; H, 7.9; N, 10.4. Found: C, 62.2; H, 8.0; N, 10.3.

5-*p*-Anisyl-1-methyl-1,6-diazonia[4.3.0]nonane Iodide (4).—A solution containing 24.2 g (0.102 mol) of **3**, 29.6 g (0.204 mol) of methyl iodide, and 500 ml of dry ether was stirred at room temperature for 15 hr. The solid was filtered off and gave 37.6 g (98%) of **4**: mp 194–197°; nmr ($CDCl_3$) δ 1.68–3.28 (9 H, series of overlapping multiplets), 3.62 (3 H, s, CH_3N^+), 3.66 (2 H, m, CH_2N^+), 3.78 (3 H, s, OCH_3), 4.32 (2 H, m, CH_2N^+), 7.10 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{15}H_{23}IN_2O$: C, 48.1; H, 6.2; N, 7.5. Found: C, 48.0; H, 6.4; N, 7.2.

1-(3-*p*-Anisoylpropionyl)hexahydropyridazine (6).—To a stirred, ice cooled solution of 50.6 g (0.243 mol) of 3-anisoylpropionic acid, 24.6 g (0.243 mol) of triethylamine, and 500 ml of dry chloroform there was added dropwise (0.7 hr; internal temperature 10 ± 5°) a solution of 26.5 g (0.243 mol) of ethyl chloroformate in 150 ml of chloroform. After stirring 1 additional hr a solution of 20.8 g (0.275 mol) of hexahydropyridazine[11] [nmr, $CDCl_3$, δ 1.68 (4 H, m, CH_2CH_2), 2.90 (4 H, m, CH_2NNCH_2), 3.38 (2 H, D_2O exchangeable, NHNH)] in 150 ml of chloroform was added dropwise (0.3 hr). The ice bath was removed and the reaction was stirred for 18 hr at room temperature, washed with 100 ml of 2 *N* Na_2CO_3 and 150 ml of water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 56.0 g (84%) of **6** as an oil: R_f 0.70 ($CHCl_3$–CH_3OH, 95:5); ir (CH_2Cl_2) 5.97 (C=O), 6.10 μ (CON); nmr ($CDCl_3$) δ 1.63 (4 H, m, CCH_2CH_2C), 2.83 (1 H, D_2O exchangeable, NH), 2.72–3.40 (5 H, m, $ARCOCH_2$, CH_2NNCH_A), 3.61 (3 H, m, CH_2CONCH_B), 3.82 (3 H, s, OCH_3), 7.42 (4 H, A_2B_2, C_6H_4).

(9) Melting points were determined on a Thomas–Hoover capillary melting point apparatus and have not been corrected. Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer and are recorded in parts per million from an internal $(CH_3)_4Si$ standard. Infrared spectrum were determined on a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectrum were carried out on a Cary Model 15 spectrometer. Mass spectra were determined on a Consolidated Electronics Co. mass spectrometer, Model 21-103C, equipped with an all-glass heated inlet. Thin layer chromatography was determined on glass plates coated with silica gel HF-254, Merck AG.

(10) G. Gever, *J. Amer. Chem. Soc.*, **76**, 1283 (1954).

(11) P. Baranger and J. Levisalles, *Bull. Soc. Chim. Fr.*, 704 (1957).

Anal. Calcd for $C_{15}H_{20}N_2O_3$: C, 65.2; H, 7.2; N, 10.1. Found: C, 65.0; H, 7.0; N, 10.0.

5-*p*-Anisyl-1,6-diazabicyclo[4.4.0]dec-4-en-2-one (7).—A mixture containing 56.0 g of **6**, 2.5 g of *p*-toluenesulfonic acid, and 750 ml of toluene was stirred and refluxed in a flask equipped with a Dean–Stark tube. After the "water" level in the side arm remained constant (18 hr) the solution was washed with 100 ml of 1 *N* Na_2CO_3 and 50 ml of water, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 33.4 g (63%) of **7**: mp 119–121° (CH_2Cl_2–diethyl ether); ir (KBr) 6.08 μ (C=O); uv maximum 246 mμ (18,300); nmr ($CDCl_3$) δ 1.68 (4 H, m, CCH_2CH_2C) 3.02 (4 H, m, CH_2NNCH_2), 3.78 (3 H, s, OCH_3), 3.83 (2 H, m, CH_2CO), 5.18 (1 H, t, J = 4 cps, HC=C), 7.12 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.7; H, 7.0; N, 10.9; O, 12.4. Found: C, 69.6; H, 7.3; N, 10.7; O, 12.3.

5-*p*-Anisyl-1,6-diazabicyclo[4.4.0]decan-2-one (8).—A mixture of 14.0 g of **7**, 0.7 g of platinum oxide and 75 ml of acetic acid was hydrogenated (50 psi; room temperature) on a Parr hydrogenation apparatus until 1 equiv of hydrogen was absorbed (2.0 hr). The catalyst was filtered off, the filtrate concentrated *in vacuo*, and the residue treated with 100 ml of 2 *N* $NaHCO_3$ and 100 ml of chloroform. The organic layer was washed with water, dried ($MgSO_4$), filtered, and concentrated to give 12.7 g (90%) of **8**: bp 220° (kugelrohr, 0.5 mm); ir (CH_2Cl_2) 6.10 μ (C=O); nmr ($CDCl_3$) δ 1.58 (4 H, m, CCH_2CH_2C), 1.90–3.50 (7 H, overlapping multiplets, CH_ANNCH_2, $ArCCH_2CH_2CO$), 3.70 (3 H, s, OCH_3), 3.92 (1 H, t, J = 5.0 cps, ArCHN), 4.28 (1 H, m, CH_BNCO), 7.08 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.2; H, 7.7; N, 10.8; O, 12.3. Found: C, 68.7; H, 8.0; N, 10.7; O, 12.5.

A solution of **8** in tetrahydrofuran was treated with anhydrous HCl to give the hydrochloride of **8**, mp 174–176°.

Anal. Calcd for $C_{15}H_{21}ClN_2O_2$: C, 60.5; H, 7.1; N, 9.4; O, 10.8. Found: C, 60.5; H, 7.5; N, 9.1; O, 11.0.

A solution of 1.0 g (0.004 mol) of **8**, 1.8 g (0.008 mol) of methyl iodide, and 60 ml of dry diethyl ether when stirred at room temperature for 52 hr (tlc gave only **8**) and refluxed for 18 hr gave after work-up only recovered **8**.

2-*p*-Anisyl-1,6-diazabicyclo[4.4.0]decane (9).—To a stirred slurry (nitrogen atmosphere) of 6.7 g (0.176 mol) of lithium aluminum hydride and 500 ml of dry diethyl ether there was added dropwise a solution of 22.8 g (0.088 mol) of **8** in 250 ml of dry diethyl ether. After 96-hr reflux the mixture was cooled in an ice bath, treated with 13.4 ml of 2 *N* NaOH, 20 ml of water, and 50 g of anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Distillation of the residue gave 17.8 (82%) of **9**: bp 205° (16 mm); mp 66–68° (pentane); nmr ($CDCl_3$) δ 1.62 (8 H, overlapping multiplets, CCH_2CH_2C, CH_2CH_2CAr), 1.90–3.32 [7 H, overlapping multiplets, $CH_2N(CH_2)N(CH_2)CHAr$], 3.73 (3 H, s, OCH_3), 7.01 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.1; H, 9.0; N, 11.4; O, 6.5. Found: C, 73.1; H, 9.3; N, 11.6; O, 6.9.

A solution of **9** in diethyl ether treated with anhydrous HCl gave the hydrochloride of **9**, mp 153–156°.

Anal. Calcd for $C_{15}H_{23}ClN_2O$: C, 63.7; H, 8.2; Cl, 12.5. Found: C, 63.5; H, 8.4; Cl, 12.7.

5-*p*-Anisyl-1-methyl-1,6-diazonia[4.4.0]decane Iodide (10).—A solution of 12.7 g (0.052 mol) of **9**, 14.7 g (0.104 mol) of methyl iodide, and 125 ml of dry diethyl ether was stirred for 50 hr at room temperature. The resultant solid was filtered off to give 18.2 g (91%) of **10**: mp 212–215° (CH_2Cl_2–ether); nmr ($CDCl_3$) δ 1.68–3.28 (11 H, overlapping multiplets, $CH_2CH_2CHNCH_2$-CH_2CH_2), 3.62 (3 H, s, CH_3N^+), 3.66 (2 H, m, $CH_AN^+CH_A$), 3.78 (3 H, s, OCH_3), 4.32 ($CH_BN^+CH_B$), 7.10 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{16}H_{25}IN_2O$: C, 49.5; H, 6.5; N, 7.2. Found: C, 49.1; H, 6.7; N, 7.2.

2-*p*-Anisyl-1,6-diazabicyclo[4.3.1]decane (12).—To a freshly prepared solution of 4.6 g (0.20 g-atom) of sodium in 150 ml of anhydrous methanol (nitrogen atmosphere) there was added a solution of 25 g (0.067 mol) of **4** in 200 ml of anhydrous methanol. After 48 hr at reflux the solvent was removed *in vacuo* and the residue treated with 100 ml of water and 150 ml of methylene chloride. The organic layer was concentrated *in vacuo* and the residue treated with 250 ml of pentane, filtered, and the filtrate concentrated *in vacuo* to give 10.6 (62%) of **12**: bp 192–195° (0.25 mm); nmr ($CDCl_3$) δ 1.05 (1 H, d-m, J = 12 cps, CH_AN), 1.50–3.56 [12 H, overlapping multiplets, $ArCH(CH_2)_3NCH_2CH_2$-CH_BN], 3.72 (3 H, s, OCH_3), 4.12 (2 H, s, NCH_2N), 7.03 (4 H, A_2B_2, C_6H_4); *m/e* 256 ($C_{15}H_{22}N_2O$).

Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.1; H, 9.0; N, 11.4. Found: C, 72.8; H, 9.1; N, 11.4.

6-*p*-Anisyl-1-methyl-1,5-diazacyclononane (13).—To a mixture of 5.0 g (0.013 mol) of **4** in *ca.* 100 ml of anhydrous ammonia, cooled in a Dry Ice–acetone bath, there was added in small portions 0.76 g (0.033 g-atom) of sodium over a 0.2-hr period. The system turned brown, then blue, and finally colorless in *ca.* 0.3 hr after the addition was completed. The ammonia was allowed to evaporate and the residue was treated with 50 ml of ice–water and then 50 ml of chloroform. The organic layer was extracted with 1 *N* HCl (50 ml, twice) and the acid layer made basic with 2 *N* NaOH, extracted with chloroform, dried ($MgSO_4$), filtered, and concentrated to give 2.8 g (87%) of **13**: bp 183–185° (0.5 mm); ir (CH_2Cl_2) 2.98 μ (NH); nmr ($CDCl_3$) δ 1.46–1.80 (4 H, m, two CH_2 groups), 1.78 (1 H, D_2O exchangeable, NH), 2.03–3.33 (8 H, m, 4 CH_2 groups), 2.32 (3 H, s, HCN_3), 3.72 (1 H, m, ArCHN), 3.75 (3 H, s, OCH_3), 7.02 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{15}H_{24}N_2O$: C, 72.6; H, 9.7; N, 11.3. Found: C, 72.4; H, 9.8; N, 11.1.

A solution of **13** in diethyl ether was treated with anhydrous HCl to give the dihydrochloride of **13**, mp 187–188° (hygroscopic).

Anal. Calcd for $C_{15}H_{26}Cl_2N_2O$: C, 56.1; H, 8.2; N, 8.7. Found: C, 56.1; H, 8.4; N, 8.8.

2-*p*-Anisyl-1,6-diaza[4.4.1]undecane (14).—To a freshly prepared solution of 1.7 g (0.074 g-atom) of sodium in 50 ml of anhydrous methanol (nitrogen atmosphere) there was added a solution of 9.0 g (0.023 mol) of **10** and 60 ml of methanol. The solution was refluxed 96 hr, concentrated *in vacuo*, and the residue treated with 75 ml of water and 75 ml of pentane. The organic layer was dried (Na_2SO_4), filtered, concentrated *in vacuo*, and distilled (kugelrohr; 1.0 mm, 200–220°) to give 4.4 g (90%) of **14** as an oil: nmr ($CDCl_3$) δ 1.33–3.27 [14 H, overlapping multiplets, $(CH_2)_3N(CH_2)_4N$], 3.70 (1 H, m, ArCHN), 3.75 (3 H, s, OCH_3), 4.08 (H_A), 4.42 (H_B, AB, J = 15.0 cps, NCH_AH_BN), 7.00 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{16}H_{24}N_2O$: C, 73.8; H, 9.3; N, 10.8. Found: C, 73.4; H, 9.5; N, 10.8.

A solution of **14** in anhydrous diethyl ether was treated with dry HCl to give the hydrochloride of **14**: mp 187–189° (hygroscopic); nmr ($CDCl_3$) δ 1.98 [8 H, m, $(CCH_2CH_2C)_2$], 2.60–3.80 [6 H, $CH_2NCN^+(CH_2)CH_2$], 3.72 (3 H, s, OCH_3), 3.81 (1 H, m, ArCHN), 4.62 (H_A), 4.93 (H_B, A_2B_2, J = 15.0 cps, $^+NCH_AH_BN$), 6.98 (4 H, A_2B_2, C_6H_4), 9.20 (1 H, D_2O exchangeable, ^+NH).

Anal. Calcd for $C_{16}H_{25}ClN_2O$: C, 61.6; H, 8.4; Cl, 12.0. Found: C, 61.7; H, 8.7; Cl, 12.3.

5-*p*-Anisyl-1-methyl-1,6-diazacyclodecane (15) and 5-*p*-Anisyl-1-methyl-1,6-diazacyclodec-4-ene (16).—Following the procedure used to prepare **13** a mixture of 9.0 g (0.023 mol) of **10**, 1.3 g (0.055 g-atom) of sodium, and ~200 ml of anhydrous liquid ammonia gave 7.2 g of basic material, R_f 0.2 and 0.5 ($CHCl_3$–CH_3OH, 90:10). Chromatography on silica gel (100 g; eluent $CHCl_3$–CH_3OH, 98:2) gave 1.8 g of **16** as an oil: R_f 0.5; ir (CH_2Cl_2) 6.05 μ (C=N); uv maxima 226 mμ (9030), 276 (1805), 283 (1435); nmr ($CDCl_3$) δ 1.63 (8 H, m, four CH_2 groups), 2.27 (3 H, s, NCH_3), 2.32 (6 H, m, CH_2NCH_2, $=NCH_2$), 3.72 (3 H, s, OCH_3), 6.98 (4 H, A_2B_2, C_6H_4) and 4.7 g of **15** as an oil, R_f 0.2; ir (CH_2Cl_2) 2.75, 3.08 and 3.13 μ (NH); nmr ($CDCl_3$ δ 1.71 (8 H, m, four CH_2 groups), 2.25 (3 H, s, NCH_3), 2.05–2.54 (6 H, m, CH_2NCH_2, N'CH_2), 3.50 (1 H, m, ArCHN), 3.71 (3 H, s, OCH_3), 5.02 (1 H, D_2O exchangeable, NH), 7.00 (4 H, A_2B_2, C_6H_4).

Anal. Calcd for $C_{16}H_{24}N_2O$: C, 73.9; H, 9.2; N, 10.8. Found: C, 73.7; H, 9.1; N, 10.6.

Registry No.—**1**, 20072-61-1; **2**, 20072-62-2; **3**, 20072-63-3; hydrochloride of **3**, 20072-64-4; **4**, 20126-07-2; **6**, 20072-65-5; **7**, 20072-66-6; **8**, 20072-67-7; hydrochloride of **8**, 20072-68-8; **9**, 20072-69-9; hydrochloride of **9**, 20072-71-3; **10**, 20072-72-4; **12**, 20072-73-5; **13**, 20072-70-2; dihydrochloride of **13**, 20072-74-6; **14**, 20072-29-1; dihydrochloride of **14**, 20072-30-4; **15**, 20072-31-5; **16**, 20072-32-6.

Acknowledgment.—The authors express their appreciation to Mr. Urs Stoeckli and his associates for instrumental and analytical data.