most equal (L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 197). The Pauling values contain contributions due to π conjugation, hyperconjugation, and changes in hybridization relative to the model compounds. We assume here a value for the π conjugation energy of acetamide of 11 kcal/mol (J. D. Roberts, R. Stewart, and M. C. Caserio, "Organic Chemistry: Methane to Macromolecules," W. A. Benjamin, New York, N. Y., 1971, p 435). This seemingly arbitrary choice represents a presumed contribution due to π conjugation that is a bit more than half of the "total resonance energy" calculated by the Pauling approach. We feel that this value represents a "safe" choice since it is approximately centered between 0 and 100% π contribution to the total resonance energy.
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(32) This value was computed by taking the experimental value of the heat of formation of dimethyl peroxide (S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 201) and adding to it the cis rotational barrier of hydrogen peroxide, *i.e.*, *E* (cis H_2O_2, dihedral angle 0°) − *E* (H_2O_2, dihedral angle at equilibrium 111°), of 7 kcal/mol [R. B. Davidson and L. C. Allen, *J. Chem. Phys.*, **55**, 519 (1971)].
(33) A value of −69 kcal/mol is obtained from ΔH_f (CH_2=$CHOCH_3$) = −27.7, ΔH_f (propene) = +0.88, and ΔH_f (isobutene) = −4.04. An alternate value of −71.8 kcal/mol is obtained from ΔH_f (CH_2=$CHOCH_3$) = −27.7, ΔH_f (CH_2=$CHCl$) = +8.5, and ΔH_f (CH_2=CCl_2) = +0.58. These two values are averaged to give the final value.
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(41) This assumes p*K* (acetanilide) ≅ p*K* $(CH_3CO)_2NH$ = 11.
(42) We obtain the heat of formation of CH_3ONHCH_3 from ΔH_f ($HONH_2$) = −32.1, ΔH_f (CH_3OCH_3) = −43.99, ΔH_f (CH_3NHCH_3) = −4.41, ΔH_f (CH_3OH) = −47.96, and ΔH_f (CH_3NH_2) = −5.49. As in the case of hydrogen peroxide (ref 32), we would add to the heat of formation of CH_3ONHCH_3 the rotational barrier contribution. In this case, the rotational barrier, *i.e.*, the energy difference between the equilibrium conformation and that which contains a pair of eclipsed hydrogens, is 1.1 kcal/mol [W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967)]. This correction is omitted as are certain other barriers which chemical experience shows to be commensurate but not precisely known. In ref 32 we explicitly included the barrier contribution for CH_3OOCH_3 since this value is exceptionally high.
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Base-Promoted Reactions of Bicyclic Mono- and Diquaternary Ammonium Salts[1]

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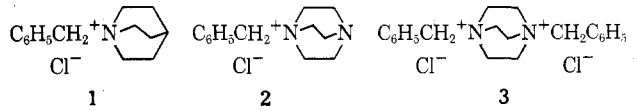
Received August 7, 1973

The synthesis and base-promoted reactions of the mono- and diquaternary ammonium salts, 1-benzyl-1-azoniabicyclo[2.2.2]octane chloride (**1**), 1-benzyl-1-azonia-4-azabiocyclo[2.2.2]octane chloride (**2**), and 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride (**3**) have been carried out. The acidifying influence of the quaternary nitrogen atom appears to be the controlling factor in determining the reaction pathway. Thus, the most acidic disalt, **3**, leads initially to an elimination product, **11**. Subsequent reaction of **11** leads to both ring expansion and vinyl migration *via* a Stevens rearrangement. Change of a bridgehead carbon atom to a bridgehead nitrogen atom (comparison of **1** and **2**) decreases the acidity and removes the elimination pathway while enhancing the Stevens rearrangement product. The novel vinyl Stevens rearrangement was confirmed by the synthesis of benzyldimethylvinylammonium hydroxide (**19**) and its conversion to α-vinylbenzyldimethylamine (**21**).

In recent years a renewed interest has been oriented toward 1,2-anionic rearrangements as new techniques and results have prompted changes in our mechanistic theories.[2] The base-promoted rearrangements of quaternary ammonium salts, the Stevens rearrangement,[3] has received considerable attention in this regard.[4] As a continuation of our interest in this area we have investigated the base-promoted reactions of the bicyclic salts 1-benzyl-1-azoniabicyclo[2.2.2]octane chloride (**1**) (quinuclidinium salt), 1-benzyl-1-azonia-4-azabicyclo[2.2.2]octane chloride (**2**) (Dabco monosalt), and 1.4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride (**3**) (Dabco disalt). In contrast to most previous work reported on the Stevens rearrangement, these bicyclic systems introduce stereochemical restraints which could influence the reaction pathways.[5] In addition to the possibility of displacement reactions, the presence of β hydrogen atoms also enables elimination to compete with the rearrangement. Another consideration in the choice of this series of compounds for study was the possibility that intramolecular electronic interactions might be important as one of the bridgehead atoms changes from C to N to N^+. Interaction between the nitrogen atoms in Dabco has been observed by esr and uv



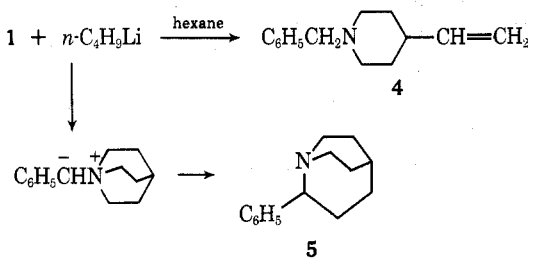
1 **2** **3**

methods.[6a] A theoretical treatment of this for Dabco and related systems has been the basis for consideration of a through bond and through space orbital overlap.[6b,c]

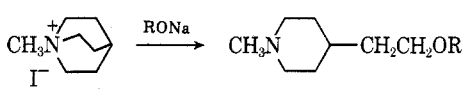
Results and Discussion

The desired quaternary ammonium salts were readily obtained through reaction of the appropriate bicyclic amine and benzyl chloride. Final traces of water were very difficult to remove from the chloride salts and in the case of the monosalts 1 and 2 it was necessary to use the tetrafluoroborate salts for final analytical data. Reactions were carried out on the chloride salts at 50–55° using an excess of strong base, *n*-butyllithium in hexane, as a heterogeneous mixture.

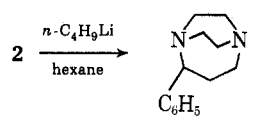
The reaction of the quinuclidinium salt 1 with *n*-butyllithium in hexane provided two major basic products. The major product (37%), 2-phenyl-1-azabicyclo[3.2.2]nonane (5), resulted from a ring-expanding Stevens rearrangement proceeding *via* the benzylammonium ylide. The second product (13%), *N*-benzyl-4-vinylpiperidine (4), resulted from a ring-opening elimination reaction.



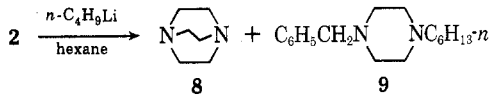
Our results can be compared with the work of Angel, *et al.*,[7] on *N*-methylquinuclidinium iodide (6). These workers reported only ring-opening displacement using alkoxides as base. They attributed the absence of elimination to the inability of obtaining an anticoplanar arrangement of a β hydrogen atom and the nitrogen atom in the bicyclic molecule. We did not observe displacement products in this work and it is probable that greater basicity relative to nucleophilicity using *n*-butyllithium in a nonpolar solvent accounts for this. It is clear that formation of the ylide required for the Stevens rearrangement in the system of Angel, *et al.*, would not be expected to be favorable using alkoxide bases.



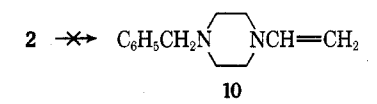
The monosalt of Dabco (2) was investigated as a model for the change of a bridgehead atom from carbon to nitrogen. We had anticipated that electronic interaction between the basic nitrogen and the quaternary nitrogen would decrease the activating effect of the positive nitrogen toward reactions with base. This was found, as the observed rate of reaction of 2 with base was slower than that of 1. It appears, however, that more than electronic effects are acting here, for the distribution of reaction pathways is different from that found with 1. A ring-expanded Stevens rearrangement product, in this case 7,



was again the major basic material formed. Three minor products can be attributed to displacement reactions. Diazabicyclo[2.2.2]octane (8-Dabco) is the result of benzyl displacement. Ring-opening displacement provided 1-benzyl-4-*n*-hexylpiperazine (9). The third minor product was



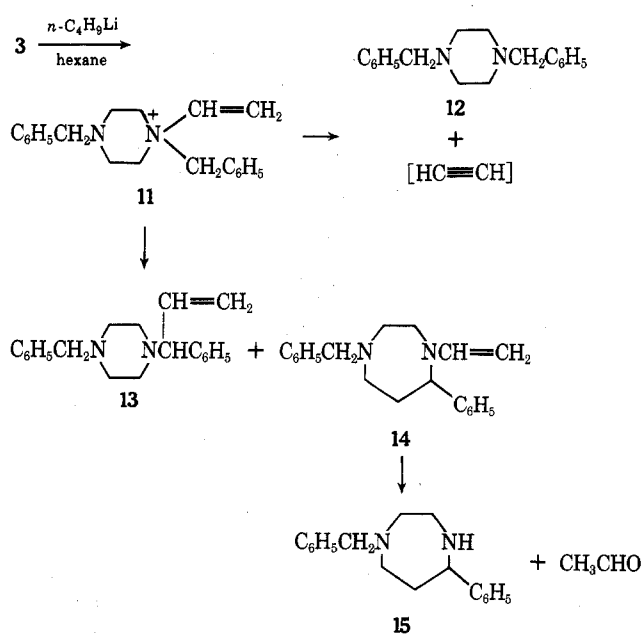
not identified but appeared to have incorporated two butyl groups on the piperazine nucleus. In contrast to 1, no elimination product (10) was observed in this system.



Being an enamine, 10 would have been hydrolyzed during work-up to acetaldehyde and *N*-benzylpiperazine, but neither of these were found.

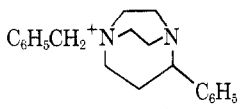
The change in reaction pathways when 2 is compared with 1 could be partly due to small conformational changes as bond lengths and possibly angles are altered. We prefer, however, to attribute the major influence to introduction of the bridgehead nitrogen atom at the 4 position, which reduces the acidity of the molecule. This has the general effect of reducing the reactivity toward base, most notably the elimination. Formation of the benzylic carbanion ylide precursor to the Stevens rearrangement becomes slower while the dispalcement reactions are little influenced by this change and become relatively more important.

The importance of substrate acidity in these reactions is clearly illustrated by the Dabco disalt 3. Treatment with *n*-butyllithium in hexane results in a rapid, somewhat exothermic reaction. The three basic products were identified as dibenzylpiperazine (12), 1-benzyl-4-(α-vinylbenzyl)piperazine (13), and 1-benzyl-5-phenylperhydro-1,4-diazepine (15). All of these can arise from the vinylammonium salt 11 formed in an initial ring-opening elimination. The major product 12 (60%) then is produced by a second elimination with the loss of acetylene. This same sequence has been observed by Hromatka and Skopalik[8] in the reaction of Dabco dimethyl disalt. The vinylammonium salt intermediate 11 also leads to a novel vinyl Stevens rearrangement product 13 (30%), and a ring-expanded



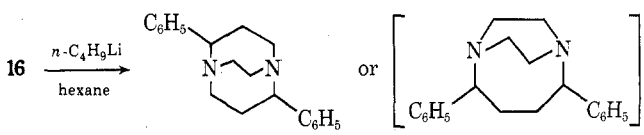
rearrangement product 14 recovered after enamine hydrolysis as 15 (10%) and acetaldehyde.

Another potential percursor to the Stevens rearrangement products 13 and 14 is 16, the result of an initial



16

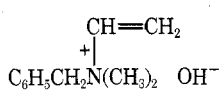
ring-expanding Stevens rearrangement. Ring-opening elimination at either the three-carbon or two-carbon bridge would provide 13 and 14, respectively. Evidence that 16 is not involved was provided through its independent synthesis (from 7) and treatment with *n*-butyllithium in hexane. This monosalt (16) rapidly reacted to give principally a second ring-expanded Stevens rearrangement product 17 (or 18). Only a small amount of 13 was found and 14 and 15 were absent.



17 18

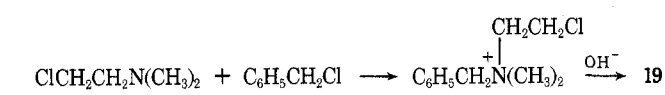
Our assignment of the structure as 17 is based on a more favorable relief of strain in the ring-expansion process and examination of models of 17 and the alternative structure 18 in relation to the spectral data obtained. The rapid reaction of 16 can be attributed to the more flexible [3.2.2] ring system, which allows the necessary migration of a two-carbon chain to the benzylic ylide carbanion. Models show that this should be more facile than in the [2.2.2] bicyclic compounds.

A vinyl rearrangement as exemplified by the conversion of 11 to 13 has never been reported for the Stevens or related 1,2-anionic rearrangements.[4a] We thus chose to investigate the parent benzyldimethylvinylammonium salt (19) to determine whether the vinyl rearrangement occurs only in the cyclic case or may be a general reaction.

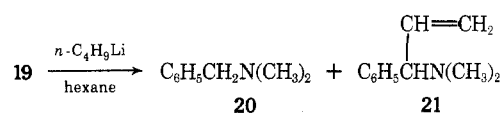


19

The desired vinylammonium salt (19) was synthesized as outlined below. Treatment of the vinylammonium salt



(19) with *n*-butyllithium in hexane provided two basic products separable by preparative gas chromatography and identified as benzyldimethylamine (20) and α-vinylbenzyldimethylamine (21). The product yields (80 and



20 21

20%, respectively) were similar to that found with the bicyclic salt 3. It therefore appears that this hitherto unknown vinyl rearrangement is expected to be general in vinylammonium systems.

Conclusions

The bicyclic mono- and diquaternary ammonium salts, when treated with strong base, may follow three reaction pathways: Stevens rearrangement, elimination, or nucleophilic displacement. It appears that relative acidity of the potentially reactive hydrogen atoms within the molecule is the dominant factor in controlling these pathways rather than small conformational changes. Thus the Dabco disalt 3 provides the most acidic β hydrogen atoms and leads initially to an elimination product. Comparison of the quinuclidinium (1) and Dabco (2) monosalts demonstrates that substitution of a nitrogen atom for a bridgehead carbon atom decreases overall acidity and removes the elimination pathway. A novel vinyl Stevens rearrangement was observed from 3 and confirmed with the parent benzyldimethylvinylammonium system 19.

Experimental Section

1-Benzyl-1-azoniabicyclo[2.2.2]octane Chloride and Fluoroborate (1). 1-Azabicyclo[2.2.2]octane [formed from 1.0 g (0.007 mol) of the hydrochloride salt] and 1.7 g (0.014 mol) of benzyl chloride were allowed to react in 25 ml of acetone. After 1 hr 1.2 g of solid was recovered. Recrystallization from absolute ethanol–ether gave white crystals, mp 241–242°. Traces of water present could not be removed by numerous methods.

The chloride salt (0.5 g) was dissolved in 10 ml of water and a saturated aqueous solution of silver fluoroborate was added until precipitation ceased. The filtrate was concentrated and cooled to give 0.5 g of solid, which was recrystallized from chloroform–ethyl acetate to give white crystals: mp 131.0–132.0°; nmr ($CDCl_3$) δ 1.7–2.3 (m, 7), 3.3–3.7 (m, 6, $^+NCH_2$), 4.40 (s, 2, $C_6H_5CH_2$), 7.44 (s, 5, C_6H_5).

Anal. Calcd for $C_{14}H_{20}NBF_4$: C, 58.15; H, 6.97; N, 4.84. Found: C, 58.33; H, 6.82; N, 4.84.

1-Benzyl-1-azonia-4-azabicyclo[2.2.2]octane Chloride and Fluoroborate (2). 1,4-Diazabicyclo[2.2.2]octane (5.6 g, 0.05 mol) and 7.5 g of benzyl chloride were allowed to react in 150 ml of acetone. The reaction was slightly exothermic. After 2 hr the precipitate was collected to give 10 g of crude product. Recrystallization from absolute ethanol–ethyl acetate gave 8 g, broad mp *ca.* 147°. Varying amounts of water present could not be removed by numerous drying procedures.

The chloride salt (1.0 g) was mixed with 3.2 g of sodium tetrafluoroborate in 25 ml of water. The solution was evaporated to dryness, and final traces of water were removed under vacuum. The solid was stirred with chloroform and the soluble material was recovered to give 1.2 g of crystalline material. Recrystallization from chloroform–ethyl acetate gave 0.9 g: mp 148.0–149.0°; nmr ($CDCl_3$) δ 3.25 (m, 12, CH_2), 4.50 (s, 2, $C_6H_5CH_2$), 7.4 (s, 5, C_6H_5).

Anal. Calcd for $C_{13}H_{19}N_2BF_4$: C, 53.82; H, 6.60; N, 9.66. Found: C, 53.59; H, 6.28; N, 9.67.

1,4-Dibenzyl-1,4-diazoniabicyclo]2.2.2[octane Dichloride (3). 1,4-Diazabicyclo[2.2.2]octane (1.1 g, 0.01 mol) and 3.7 g (0.03 mol) of benzyl chloride in 15 ml of absolute ethanol were refluxed for 2 hr. After cooling, ether was added to precipitate the product, giving 2.5 g of white solid. Recrystallization from absolute ethanol–ether gave crystals: mp 240° dec; nmr (D_2O) δ (from external TMS) 3.95 (s, 12, $^+NCH_2$), 4.74 (s, 4, $C_6H_5CH_2$), 7.55 (s, 10, C_6H_5).

Anal. Calcd for $C_{20}H_{26}N_2Cl_2$: C, 65.75; H, 7.17; N, 7.67. Found: C, 65.53; H, 7.20; N, 7.35.

Benzyldimethylvinylammonium Hydroxide and Fluoroborate (19). *N*-β-Chloroethyldimethylamine hydrochloride (1.0 g) was dissolved in 5 ml of distilled water and 10 ml of chloroform was added. Sodium hydroxide (6 *N*) solution was added until the aqueous layer gave an alkaline reaction, the mixture was shaken, and the chloroform layer was separated. The aqueous layer was extracted a second time with chloroform (10 ml), and the combined chloroform extracts were dried over magnesium sulfate. Benzyl chloride (1 ml) was added to the chloroform solution and heated to 45° for 16 hr. The solvent and volatile starting material were removed under vacuum to give benzyl(β-chloroethyl)dimethylammonium chloride (1.2 g) as a white, hygroscopic solid: nmr (D_2O) δ (from external TMS) 3.15 [s, 6, $N(CH_3)_2$], 3.77 (t, J = 5.5 Hz, 2, NCH_2), 4.10 (t, J = 5.5 Hz, 2, CH_2Cl), 4.58 (s, 2, $C_6H_5CH_2$), 7.55 (s, 5, C_6H_5).

The chloro salt (0.5 g) was dissolved in water (1 ml) and sodium fluoroborate in water (10 ml, 30%) was added. An oil was precipitated which rapidly crystallized. It was filtered off and recrystallized from acetone–chloroform, mp 96–97°.

Anal. Calcd for $C_{11}H_{17}NClBF_4$: C, 46.27; H, 6.00; N, 4.91. Found: C, 46.22; H, 6.03; N, 4.76.

Benzyl(β-chloroethyl)dimethylammonium chloride (1.0 g) was dissolved in distilled water (10 ml) and introduced onto a column of Amberlite ion exchange resin (IRA 4015) in the hydroxide form (length 135 mm, diameter 0.20 mm). The solution was allowed to remain in contact with the resin for 10 min and was then eluted with water and the column was washed further with water until the eluate was no longer alkaline. The total eluate was then evaporated to give solid **19**: nmr (D_2O) δ 3.25 [s, 6, $N(CH_3)_2$], 5.5 (m, 2, $=CH_2$), 6.5 (m, 1, $=CH$), 6.65 (s, 2, $C_6H_5CH_2$), 7.55 (s, 5, C_6H_5).

The hydroxide salt (**19**) prepared from 0.5 g of chloride was dissolved in a minimum amount of water and 10 ml of 30% sodium fluoroborate was added. The oil which precipitated solidified upon drying and was recrystallized from acetone–chloroform, mp 75.5–77.0°.

Anal. Calcd for $C_{11}H_{16}NBF_4$: C, 53.05; H, 6.48; N, 5.62. Found: C, 52.79; H, 6.46; N, 5.72.

Reaction of 1. The chloride salt (1.0 g, 4×10^{-4} mol) was stirred with 6 ml of 1.6 *M* *n*-butyllithium in hexane (1×10^{-2} mol) under nitrogen at 50° for 20 hr. The reaction mixture was cooled and 15 ml of water was carefully added. Recovery of the basic material using dilute hydrochloric acid and regeneration with dilute sodium hydroxide gave 0.4 g of chloroform-soluble yellow oil. The original aqueous phase gave *ca.* 0.5 g (50%) of unreacted starting material. The basic oil, shown to be two components by tlc, was separated by column chromatography on grade II alumina using 30–60° petroleum ether with increasing concentrations of ether. The minor component (0.1 g) eluted first and was identified as **4**: nmr (CCl_4) δ 1.3–3.0 (m, 9), 3.42 (s, 2, $C_6H_5CH_2$), 4.84, 4.90 (m, 2, $=CH_2$), 5.75 (m, 1, $=CH$), 7.22 (s, 5, C_6H_5).

The slower moving component (0.3 g) was identified as **5**: nmr (CCl_4) δ 1.2–2.3 (m, 9), 2.6–3.3 (m, 4, NCH_2), 3.78 (d of d, J = 5, 10 Hz, 1, C_6H_5CH), 7.0–7.4 (m, 5, C_6H_5).

Anal. Calcd for $C_{14}H_{19}N$: C, 83.59; H, 9.45; N, 6.96. Found: C, 83.78; H, 9.47; N, 7.27.

Reaction of 2. The chloride salt (0.25 g, 1×10^{-3} mol) and 3.2×10^{-3} mol of *n*-butyllithium in 12 ml of hexane was stirred under nitrogen at 50–55° for 3 days. After cooling, water was carefully added and 0.1 g of brown oil was collected from the hexane layer. Partition of this oil between 1 *N* hydrochloric acid and chloroform ultimately yielded 0.05 g of basic materials. Additional rearrangement product **7** could be obtained from the aqueous layer (along with **8**) by partitioning between chloroform and water. The mixed basic materials were purified by column chromatography on grade III alumina using petroleum ether–ether as eluent. The first component eluted was not identified. The second component was identified as **9**: nmr (CCl_4) δ 0.7–1.8 (m, 11, *n*-C_5H_{11}), 1.9–2.8 (m, 10 NCH_2), 3.42 (s, 2, $C_6H_5CH_2$), 7.2 (m, 5, C_6H_5). The third component was identified as **7**: nmr (CCl_4) δ 1.6–3.7 (m, 4), 2.7 (m, 4), 2.96 (s, 4) 3.89 (d of d, J = 5.5, 11.5 Hz, 1, C_6H_5CH), 7.2 (m, 5, C_6H_5). Methiodide crystallized from absolute ethanol: mp 193–195° dec; nmr (D_2O) δ (external TMS) 3.25 (s, 3, $^+NCH_3$), 2.0–4.1 (m, 12), 4.32 (d of d, J = 5, 12 Hz, 1, C_6H_5CH), 7.45 (s, 5, C_6H_5).

Anal. Calcd for $C_{14}H_{21}N_2I$: C, 48.71; H, 6.42; N, 8.11. Found: C, 48.84; H, 6.14; N, 7.95.

Unreacted starting material and **8** were identified by their nmr spectra.

Reaction of 3. To the dichloride (0.60 g, 1.6×10^{-3} mol) in 15 ml of hexane was added 6 ml (1×10^{-2} mol) of 1.6 *N* *n*-butyllithium in hexane. The mixture spontaneously warmed and after 0.5 hr was further heated at 50° for an additional 1 hr. Work-up as above gave 0.52 g of basic products which could be separated by column chromatography on silica gel. The first component (0.15 g) was eluted using 20% ether in petroleum ether (bp 60–80°) and was identified as **13**: nmr (CCl_4) δ 2.37 (s, 8, CH_2), 3.40 (s, 2, $C_6H_5CH_2$), 3.58 (d, J = 8 Hz, 1, CH), 4.97, 5.10 (m, 2, $=CH_2$), 5.86 (m, 1, $=CH$), 7.18 (s, 5, C_6H_5). The methiodide crystallized from acetone: mp 202–203° dec; nmr ($CDCl_3$) δ 2.0–4.0 (m, 8, CH_2), 3.30 (s, 3, CH_3), 3.98 (d, J = 8 Hz, 1, C_6H_5CH), 5.16 (s, 2, $C_6H_5CH_2$), 5.0–6.2 (m, 3, $CH=CH_2$), 7.30 (s), and 7.2–7.8 (m) (total 10).

Anal. Calcd for $C_{21}H_{27}N_2I$: C, 58.07; H, 6.22; N, 6.45. Found: C, 58.27; H, 6.35; N, 6.24.

The second component (0.30 g) was eluted with ether and identified as **12**: mp 89.0–90.0° (reported mp 92°);[9] nmr (CCl_4) δ 2.38 (s, 8, NCH_2), 3.42 (s, 4, $C_6H_5CH_2$), 7.17 (s, 10, C_6H_5).

The third component (0.05 g) was eluted with methanol and identified as **15**: nmr (CCl_4) δ 1.5–3.0 (m, 10, ring H's, NH), 3.44 (s, 2, $C_6H_5CH_2$), 7.0–7.5 (m, 10, C_6H_5). This oil formed a *p*-toluenesulfonamide which was an oil. In a separate run, acetaldehyde was identified as its 2,4-dinitrophenylhydrazone.

Preparation and Reaction of 16. The reaction of **7** and benzyl chloride in acetone overnight gave an insoluble oil which slowly solidified on further washing with acetone. Recrystallization from acetone–chloroform gave **16**, yellow crystals, mp 185°, which was not purified further, nmr (D_2O) δ 2.2–4.3 (m, 13), 5.1 (s, 2, $C_6H_5CH_2$), 7.1–7.9 (m, 10, C_6H_5).

The chloride salt **16** (0.16 g, 0.5×10^{-3} mol) in 10 ml of hexane was stirred with 2.5×10^{-3} mol of *n*-butyllithium under nitrogen at 55° for 2 hr. Work-up gave 0.15 g of colorless oil which was crystallized from cold petroleum ether to give **17** as yellow crystals: mp 109–110°; nmr (CCl_4) δ 1.9–3.4 (m, 12), 4.0 (t, 9, C_6H_5CH), 7.0–7.5 (m, 10, C_6H_5). In addition a small amount of **13** was found, confirming the structural assignment for **16**.

Reaction of 19. Benzydimethylvinylammonium hydroxide (from 1.0 g of chloro salt, 4.6×10^{-3} mol) was suspended in 50 ml of *n*-hexane, and 8 ml of 1.6 *M* *n*-butyllithium solution in hexane (13×10^{-3} mol) was added with stirring. The mixture was heated 45–50° under reflux overnight and after cooling, water (10 ml) was added dropwise. The basic products were recovered as a yellow oil and separated by gas chromatography using 8 ft of Carbowax 20 M on Chromosorb 60–80 WAW at 150°. The two components were identified as benzyldimethylamine (**20**) and α-vinylbenzyldimethylamine (**21**): nmr (CCl_4) δ 2.1 [s, 6, $N(CH_3)_2$], 3.45 (d, J = 8 Hz, 1, C_6H_5CH), 5.0 (d of d, J = 2, 9 Hz), and 5.1 (d of d, J = 2, 17 Hz, 2, $=CH_2$), 5.9 (d of d of d, J = 8, 9, 17 Hz, 1, $=CH$), 7.19 (s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 82.10; H, 9.23; N, 8.80.

Registry No. **1**, 42790-41-0; **1** fluoroborate, 42790-20-5; **2**, 42790-42-1; **2** fluoroborate, 42790-21-6; **3**, 42790-43-2; **4**, 42790-44-3; **5**, 42790-45-4; **7**, 42790-46-5; **7** methiodide, 42790-47-6; **9**, 42992-87-0; **12**, 1034-11-3; **13**, 42790-49-8; **13** methiodide, 42790-50-1; **15**, 42790-51-2; **16**, 42790-52-3; **16** chloride salt, 42790-53-4; **17**, 42992-88-1; **19** hydroxide, 42790-54-5; **19** fluoroborate, 42790-22-7; **20**, 103-83-3; **21**, 42790-56-7; 1-azabicyclo[2.2.2]octane, 100-76-5; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; *N*-β-chloroethyldimethylamine hydrochloride, 4584-46-7; benzyl(β-chloroethyl)dimethylammonium chloride, 42790-57-8.

References and Notes

(1) Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.
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