(N=N), 1440 (NO), 1215 (CO).

Anal. Calcd for $C_9H_{14}BrClN_2O_3$: C, 34.41; H, 4.51; N, 8.93; total halogen, 36.78. Found: C, 34.41; H, 4.47; N, 8.94; total halogen, 36.58.

B. Cuprous Cyanide as Promoter.[5] A mixture of nitroso compound **4** (2.27 g, 0.01 mol), *N,N*-dichlorourethane (1.68 g, 0.01 mol), CuCN (1.79 g, 0.02 mol), and CH_3CN (60 mL) was stirred at 0 °C (color change from olive green to black). The reaction mixture was warmed to room temperature, stirred overnight, added to 300 mL of H_2O, and then repeatedly extracted with ether until the aqueous layer was light blue. The ether extract was washed once with saturated aqueous NaCl and dried ($CaCl_2$), and the ether was evaporated. The remaining yellow green oil was chromatographed [Skelly B–benzene (7:3 (v/v)) on silica] providing 1.37 g (44% of theory) of **6**.

***N*-Carbethoxy-*N'*-(1-chloro-2-bromocyclohexyl)diazene *N'*-Oxide (12).** The procedure described for **6** was used with $CuBr_2$ promoter: 62% yield of white solid; mp 30–31 °C; NMR ($CDCl_3$) δ 3.10–0.95 (m, aliphatic), 1.39 (t, 3.2, OCH_2CH_3), 4.42 (q, 2.2, OCH_2CH_3), 5.00 (t, 1, CHBr); IR (CCl_4) 1755 (C=O), 1505 (N=N), 1430 (NO), 1210 (CO).

Anal. Calcd for $C_9H_{14}BrClN_2O_3$: C, 34.41; H, 4.51; N, 8.93. Found: C, 34.36; H, 4.45; N, 8.90.

Dehalogenation. With Sodium Iodide.[21] Azoxy compound (**6** or **12**) (0.26 g, 8.3×10^{-4} mol) was stirred in 20 mL of dry acetone at 0 °C with a large excess (1.2 g) of NaI. Compound **6** was stirred for 6 h; compound **12** was warmed to room temperature and stirred for 72 h. Workup consisted of adding the reaction mixture to ether (60 mL) and washing once with dilute aqueous $Na_2S_2O_3$ and then once with saturated aqueous NaCl. The ether phase was dried (Na_2SO_4) and the solvent was evaporated. Compound **6** yielded 0.16 g (96% of theory) of the dehalogenated product **7**: bp 110 °C (0.25 mm); NMR ($CDCl_3$) δ 2.9–1.2 (m, aliphatic), 1.38 (t, 3.2, OCH_2CH_3), 4.40 (q, 2.1, OCH_2CH_3), 7.22 (m, 1, C=CH); IR (neat) 1755 (C=O), 1670 (C=C), 1480–1430 (N=N, NO), 1220 (C—O), 925, 855 (C=C).

Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.26; H, 7.17; N, 14.32.

Compound **12** did not undergo reaction and was recovered.

(21) A. J. Solo and B. Singh, *J. Org. Chem.*, **30**, 1658 (1965).

With Cuprous Chloride/Ammonium Hydroxide. A procedure similar to a literature one was used.[22] Azoxy compound **6** (0.25 g, 8.0×10^{-4} mol) and CuCl (0.16 g, 1.6×10^{-3} mol) were stirred in CH_3CN (9 mL) at 0 °C. Addition of aqueous NH_4OH (10%, 3 mL) over a 5-min period caused the faint yellow solution immediately to turn dark blue. The reaction mixture was warmed to room temperature and after 4 h was added to 70 mL of $CHCl_3$. Water (15 mL) was added and the phases were separated. The $CHCl_3$ phase was washed to neutral pH with H_2O and dried (Na_2SO_4), and the solvent was evaporated to yield 0.11 g (69% of theory) of **7**.

With Zinc/Acetic Acid. A procedure similar to a published one was used.[9] Azoxy compound **6** (0.26 g, 8.31×10^{-4} mol) and powdered Zn (0.1 g, large excess) were stirred with 25 mL of a solution of ether–30% (w/w) aqueous acetic acid (25:1 (v/v)) at 0 °C. After 8 h the reaction mixture was added to CH_2Cl_2 (100 mL), the solid was filtered, the CH_2Cl_2 solution was dried (Na_2SO_4), and solvent was evaporated. Preparative TLC (CH_2Cl_2 on silica) was carried out on the remaining oil to yield **7** (42 mg, 26% of theory).

Attempted with Triphenylphosphine. A procedure similar to a published one was used.[23] Azoxy compound **6** (0.26 g, 8.3×10^{-4} mol) was stirred in dry ether (17 mL) at 0 °C. To this was added an equimolar amount of Ph_3P (0.27 g) in 10 mL of ether. Immediately upon addition, a white solid precipitated. After 30 min, TLC indicated that all of the Ph_3P had been consumed. After the solid was filtered, solvent was evaporated. Spectral evidence indicated that the desired product **7** was not present.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **2**, 822-87-7; **3**, 3238-18-4; **4**, 70224-62-3; **5**, 13698-16-3; **6**, 70224-63-4; **7**, 70224-64-5; **8**, 108-94-1; **9**, 822-85-5; **10**, 70224-65-6; **11**, 70224-66-7; **12**, 70224-67-8; NaI, 7681-82-5; CuCl, 7758-89-6; NH_4OH, 1336-21-6; Zn, 7440-66-6; HOAc, 64-19-7; Ph_3P, 603-35-0.

(22) K. A. Kurginyan, R. G. Karapetyan, and G. A. Chakhadzhyan, *Arm. Khim. Zh.*, **27**, 1065 (1974); *Chem. Abstr.*, **82**, 139177 (1975).

(23) C. J. Devlin and B. J. Walker, *J. Chem. Soc., Perkin Trans. 1*, 1249 (1972).

Reactions of Alkylbenzyldimethylammonium Halides with Amide in Liquid Ammonia

Carl L. Bumgardner,* Hon-Bin Hsu, F. Afghahi, William L. Roberts, and Suzanne T. Purrington

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

Received March 19, 1979

Competitive elimination and rearrangement reactions of alkylbenzyldimethylammonium ions with amide ion in liquid ammonia have been investigated. Elimination is largely dependent on the geometry of the alkyl group. Cyclohexyl- and *tert*-butylbenzyldimethylammonium halides undergo more Stevens than Sommelet–Hauser rearrangement with amide ion in liquid ammonia. The results are interpreted in light of the reactivity of the intermediate ylide. The structure of the rearrangement product from isopropylbenzyldimethylammonium iodide has been reassigned.

When treated with base, quaternary ammonium salts may undergo various reactions. If the salt contains a hydrogen atom β to the nitrogen atom, elimination to produce an alkene usually is important. Under certain conditions a γ proton may be removed resulting in formation of a cyclopropane derivative.[1] Base may also abstract a proton α to the nitrogen atom forming an ylide which in certain cases can isomerize to a tertiary amine.[2]

In the case of benzyltrimethylammonium ion two ylides are possible, one resulting from removal of a proton from a methyl group and one from the benzyl position.[3] The ylide generated by the latter process merely returns to starting material, whereas the methyl ylide may isomerize by two different pathways—the Stevens rearrangement[4]

(1) C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4420 (1961).

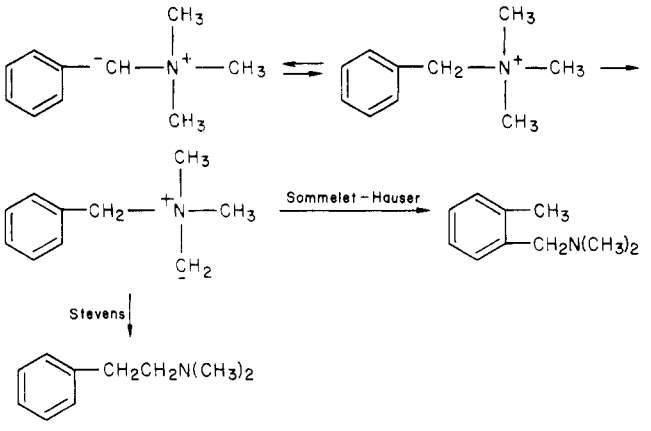
(2) For an excellent review, see S. H. Pine, *Org. React.*, **18**, 403 (1970).

(3) W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1108 (1964).

(4) T. S. Stevens, E. M. Creighton, A. B. Gorden, and M. Mac Nicol, *J. Chem. Soc.*, 3193 (1928).

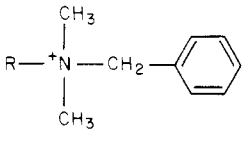
0022-3263/79/1944-2348$01.00/0

Scheme I



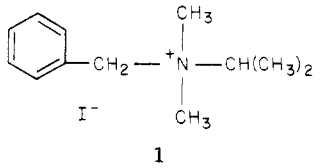
(1,2 migration) and the Sommelet–Hauser rearrangement[5,6] (ortho substitution) (Scheme I).

Both processes can occur simultaneously under certain conditions. If one of the methyl groups in the benzyltrimethylammonium halide is replaced by a different substituent, rearrangement can proceed by different ylides which lead to isomeric products.[2] Results from a previous study indicate that for substituted ions

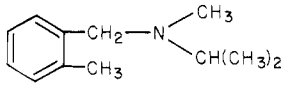


where the alkyl substituent R is allyl, benzyl, or cyclopropylcarbinyl,[7] the major product is derived from the ylide which is stabilized by interaction with the adjacent centers. When the alkyl substituent R is ethyl or isobutyl,[8] there is no stabilization of the α carbanion; the methyl ylide is the precursor of the major product. This difference offers an opportunity to study features in alkyl substituents which influence the mode of rearrangement. We have examined the effect of various alkyl groups on the course of the reaction of alkylbenzyldimethylammonium ions with amide ion in liquid ammonia.

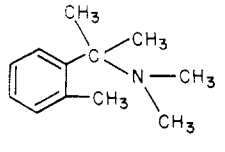
When the base system is NH_2^- in NH_3(l), the implication has been that the Sommelet–Hauser reaction is the exclusive or main rearrangement pathway.[2] For example, Jones and Hauser[8] reported that the reaction of isopropylbenzyldimethylammonium iodide (1) with $NaNH_2$–NH_3(l) gave elimination (10–11%) and both of the possible Sommelet–Hauser products (82–83%) [*N*-methyl-*N*-isopropyl-α-amino-*o*-xylene (2) and *N*,*N*-dimethyl-α,α-dimethyl-α-amino-*o*-xylene (3)] but no 1,2-migration product.



1



2



3

(5) M. Sommelet, *C. R. Hebd. Seances Acad. Sci.*, **205**, 56 (1937).
(6) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).
(7) C. L. Bumgardner, *J. Am. Chem. Soc.*, **85**, 73 (1963).
(8) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 1542 (1962).

Table I. Relative Product Yields from Quaternary Salt Reaction With Amide Ion

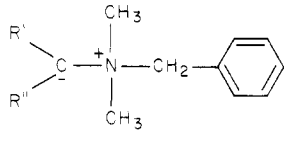
	R	M^+	X^-	elimination	Sommelet-Hauser	Stevens
1	isopropyl[b]	Na	I	12	88	
1	isopropyl[b]	Na	I	11	89	
1a	isopropyl	K	Br	58	11	31
1b	isopropyl	K	Br	78	5	17
1c	isopropyl[c]	Na	I	61	17	21
1d	isopropyl[d]	Na	I	68	9	13
4	cyclopropyl[a]	Na	Br	33	67	
5	cyclobutyl	Na	I	3	97	
6	cyclopentyl	K	Br	93	1.6	5.6
7a	cyclohexyl	K	Br	30	23	47
7b	cyclohexyl	Na	Br	31	23	46
8	cycloheptyl	K	Br	95	1	3.6
9	cyclooctyl	K	Br	96	1	3.4
10	*tert*-butyl[e]	Na	Br	14	6	62
11	ethyl-β-d_3	Na	I	24	(63 + 13)[f]	
12	cyclopropylcarbinyl[g]	Na	Br		(73 + 18)[f]	9
13	cyclobutylcarbinyl	Na	Cl	24	(58 + 18)[f]	
14	*trans*-2-phenylcyclopropyl	K	Br	100		
15	*cis*-2-phenylcyclopropyl	Na	I	97		3

[a] Reference 12. [b] Reference 8. [c] Reaction run at −77 °C. [d] Dimer **16** was isolated in 9% relative yield. [e] Dimer **16** was isolated in 18% relative yield. [f] Two Sommelet-Hauser products were isolated; the methyl ylide precursor predominates. [g] Reference 7.

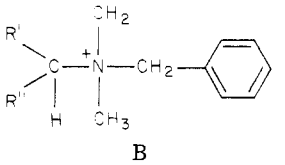
In light of our observations of the reaction of various alkylbenzyldimethylammonium salts in liquid ammonia, we questioned the nature of product **3**. Consequently, we repeated the reaction and have found that only one Sommelet–Hauser product is formed.

Results and Discussion

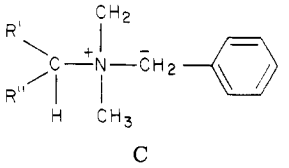
The relative product yields for the reactions of various quaternary ammonium compounds with amide ion in liquid ammonia are summarized in Table I. Except when the alkyl substituent is *tert*-butyl, three possible ylide intermediates, A, B, and C, can be postulated. When the



A



B



C

alkyl substituent is secondary (R′, R″ ≠ H), the ylide intermediate A contains an unfavorable tertiary anionic site. Consequently the cycloalkyl and isopropyl salts, **1** and **4–9**, do not give rise to type A ylides (R′, R″ ≠ H) or to products derived from them. When the alkyl substituent is primary as in salts **11–13**, a type A intermediate (R′ = H, R″ ≠ H) is involved as evidenced by the presence of two Sommerlet–Hauser rearrangement products, one from a type A ylide and one from a type B ylide. The minor Sommerlet–Hauser products obtained from salts **11–13** go through a type A intermediate containing a secondary anionic site. When the R substituent is primary

and contains electron-delocalizing groups such as phenacyl,[4] the type A ylides are so stable that the Sommerlet–Hauser reaction does not occur.

Type B ylides are statistically the most favored because, in the starting material, there are six methyl protons. These ylides are also undoubtedly the most reactive and are present in very low concentrations.[9] From salts containing secondary alkyl substituents there is only one Sommelet–Hauser product observed and it arises via intermediate ylide B. Similarly, the major Sommerlet–Hauser product arising from salts with primary substituents involve type B ylides.

The type C ylide, a benzylic carbanion, is formed reversibly.[3] It is the most stable and least reactive ylide species in the system. Sommelet–Hauser reactions do not occur from type C ylides except in the special case of dibenzyldimethylammonium ions.[6]

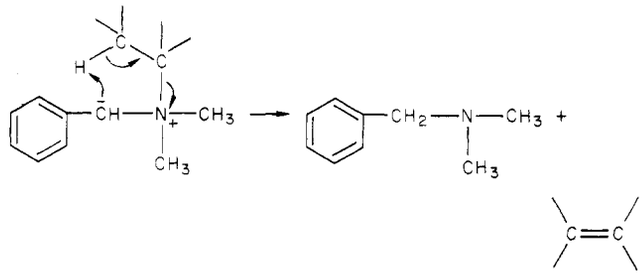
Intramolecular elimination reactions can proceed through type C ylides. When (ethyl-β-d_3)benzyldimethylammonium iodide (**11**) was treated with sodium amide, more than 90% of the deuterium lost during elimination was found by NMR to be on the benzylic carbon in the isolated benzyldimethylamine. This result, substantiated by mass spectra data, shows that α'–β elimination occurs primarily from the most stable ylide intermediate (C).

In contrast, elimination of trimethylamine from cycloalkyltrimethylammonium salts[10] and from (β,β-dideuterio-β-phenylethyl)trimethylammonium bromide[11] proceeds by a normal E2 elimination. It is the increased acidity of the benzylic proton that causes the α'–β process to predominate.

The α'–β elimination, a syn process, is most favorable when a planar transition state is achieved[12] (Scheme II). This geometric constraint makes the elimination reaction extremely sensitive to ring size. Elimination from the cyclopropyl salt (**4**) is competitive with the Sommelet–Hauser rearrangement. Elimination is facile because the cis β hydrogen and the nitrogen are eclipsed, a favorable relation for the operation of the α'–β process.[12] Elimination from both *cis*- and *trans*-(2-phenylcyclopropyl)benzyldimethylammonium bromide, **14** and **15**, gives benzyldimethylamine and poly(phenylcyclopropene) in almost quantitative yield; no Stevens product is formed. These results are consistent with a marked increase in acidity of the proton at the 2 position of the cyclopropyl ring due to the presence of the phenyl substituent. That the *cis*-2-phenylcyclopropyl salt (**15**) undergoes almost exclusive elimination suggests that direct anti elimination takes place.[13] The fact that a cyclopropene is produced so readily under these low-temperature conditions suggests that such eliminations could be used for the synthesis of more heavily substituted cyclopropenes.

The cyclobutyl salt (**5**) undergoes practically no elimination because a planar transition state cannot be achieved easily. Elimination by an E2 pathway, although possible, does not occur, because the Sommelet–Hauser rearrangement competes readily under the reaction conditions.

Scheme II



Elimination from the cyclooctyl salt (**9**) gives rise to *cis*-cyclooctene.[14] This result is consistent with that obtained by Sicher, Závada, and Krupička[15] for the decomposition of cyclooctyldimethylamine oxide, a reaction known to be an α'–β elimination.

It is also not surprising to find that cyclohexylbenzyldimethylammonium bromide (**7**) undergoes relatively little elimination. The staggered arrangement of the hydrogen and nitrogen makes it difficult to attain a planar transition state. Since the benzylic ylide (C) is not geometrically set up to undergo α'–β elimination, rearrangement competes successfully. Both Stevens and Sommelet–Hauser products are obtained in considerable quantities.

These results may be rationalized by the reaction pathway shown in Scheme III where the Stevens rearrangement entails homolytic cleavage of the ylide into a neutral nitrogen-containing radical and an alkyl radical.[16] A review of the literature[2] leads us to generalize that the Stevens rearrangement is competitive with the Sommelet–Hauser rearrangement in liquid ammonia only for those salts which can form a secondary, tertiary, or resonance-stabilized radical. We have observed no case where a methyl ylide gives rise to a Stevens rearrangement because the Sommelet–Hauser rearrangement involving this ylide competes so successfully. (See Scheme III, eq 1 and 2.) The absence of a Stevens product can be predicted from the extremely low steady-state concentration of methyl ylide[9] coupled with a low rate constant for the Stevens rearrangement. The benzyl ylide, present in much greater concentration, is able to undergo the Stevens rearrangement (eq 3).

The Sommelet–Hauser rearrangement (eq 1) is believed to involve concerted isomerization of an ylide to an exo-methylene intermediate which is the precursor of the final product. Orbital symmetry can be maintained during the concerted six-electron transformation in the ground state. However, the Stevens rearrangement (eq 3) involves four electrons and should not be concerted in the ground state because orbital symmetry cannot be maintained during the front-side migration. This reaction becomes competitive when homolytic cleavage of the ylide produces a secondary or tertiary radical.[17] However, when the alkyl

(9) Adduct formation between the methyl ylide and benzophenone is not observed; however, in the same system reaction from the methyl ylide is observed.[3]

(10) A. N. Bourns and P. J. Smith, *Proc. Chem. Soc., London*, 366 (1964).

(11) G. Wittig and T. F. Burger, *Justus Liebigs Ann. Chem.*, **632**, 85 (1960).

(12) C. L. Bumgardner, *J. Am. Chem. Soc.*, **88**, 5515 (1966).

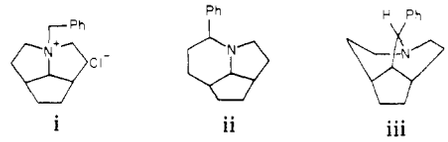
(13) Epimerization of the phenyl ring on the cyclopropyl ring is likely to be a slow process. Cyclopropyl isonitriles maintain their configuration in aprotic solvents at low temperature (H. M. Walborsky and M. P. Periasamy, *J. Am. Chem. Soc.*, **96**, 3711 (1974); **97**, 5930 (1975)).

(14) C. L. Bumgardner, *J. Org. Chem.*, **27**, 1035 (1962).

(15) J. Sicher, J. Závada, and J. Krupička, *Tetrahedron Lett.*, 1619 (1966).

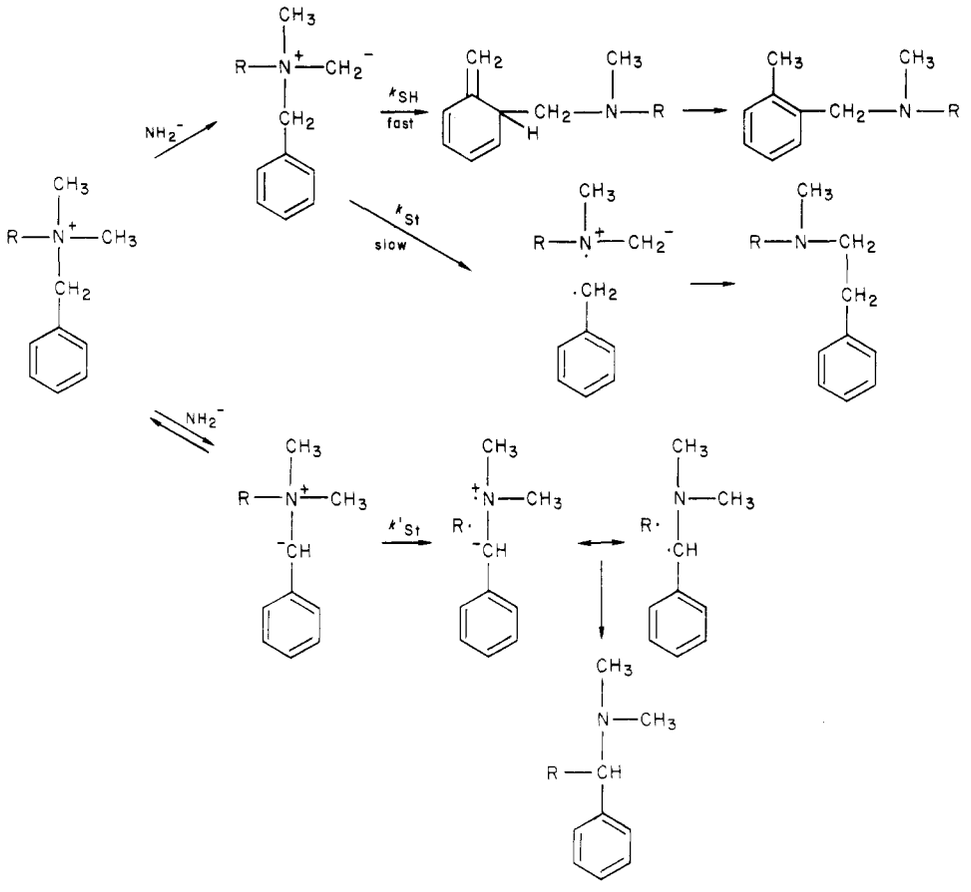
(16) J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Commun.*, 31 (1970).

(17) The recent report of a Stevens rearrangement which apparently occurred via a primary radical intermediate is inconsistent with these observations. A. G. Anderson, Jr., and P. C. Wade, *J. Org. Chem.*, **43**, 54 (1978), report that quaternary salt i gives ii on the basis of NMR integral data. However, the isomeric tertiary amine iii requiring the intermediacy of a secondary radical is not rigorously excluded.



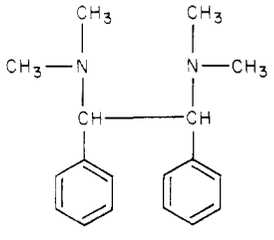
i ii iii

Scheme III



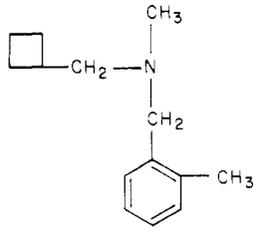
substituent is cyclopropyl or cyclobutyl (**4** or **5**), relatively high-energy secondary radicals[18] are required for the Stevens reaction, so the rate of the reaction (k'_{St}) falls and the Stevens route is not competitive. The view that the Stevens rearrangement actually proceeds by dissociation of the ylide into radicals[16] has been substantiated by CIDNP studies and is in harmony with the temperature effect. The stepwise Stevens route has a higher $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ than the concerted Sommelet–Hauser process.[19]

Treatment of the *tert*-butyl salt (**10**) with amide ion in liquid ammonia gives one elimination, one Sommelet–Hauser, and one Stevens product and dimer **16**. The yield of Stevens product is much larger than for salts containing secondary alkyl groups because of the greater stability of tertiary radicals relative to secondary. Dimer **16** is formed by coupling of aminobenzylic radicals.

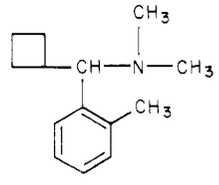


16

The cyclobutylcarbinylbenzyldimethylammonium ion (**13**) undergoes Sommelet–Hauser rearrangement mainly from the methyl ylide to give *N*-cyclobutylcarbinyl-*N*-methyl-*o*-xylylamine (**17**). The ratio of compound **17** to α-cyclobutyl-*N*,*N*-dimethyl-*o*-xylylamine (**18**) is virtually



17



18

statistical, i.e., 3:1 in favor of the methyl ylide route, and contrasts with results obtained from cyclopropylcarbinylbenzyldimethylammonium bromide (**12**) where a reaction pathway involving a carbinyl ylide is favored. We interpret these results as indicating that the cyclobutyl ring is not able to stabilize an adjacent negative charge. Furthermore, since cyclobutylcarbinyl radicals show no special stabilization due to the small ring, it is consistent that no Stevens rearrangement product is observed.

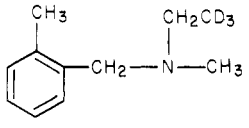
The alkyl group of the alkylbenzyldimethylammonium salts, therefore, very largely determines the major products of the reaction with base. When the alkyl group is methyl, reaction proceeds only through the methyl ylide (B) to form Sommelet–Hauser products. In the case of a primary alkyl group, one elimination and two Sommelet–Hauser products are possible; all are formed.[8] In general, no Stevens product is formed because the radical-pair intermediate would include a primary radical site. Thus, the (ethyl-β-d_3)benzyldimethylammonium iodide (**11**) gives no Stevens rearrangement product.

When the alkyl group is secondary, elimination is accompanied by Stevens rearrangement through the benzylic

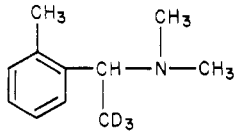
(18) D. E. Applequist and J. H. Klug, *J. Org. Chem.*, **43**, 1729 (1978).
(19) A. G. Guimanini, C. Tombini, G. Lercker, and A. R. Lepley, *J. Org. Chem.*, **41**, 2187 (1976).

ylide (C) and Sommelet–Hauser rearrangement through the methyl ylide (B).

One might, therefore, conclude that, in the absence of special stabilization,[20] type A ylides (R′, R″ ≠ H) are not formed. The Sommelet–Hauser reaction proceeds only from a methyl ylide (B) or secondary type A ylide (R′ = H, R″ ≠ H). This selectivity is verified in the case of the (ethyl-β-d_3)benzyldimethylammonium salt where two Sommelet–Hauser products, **19** and **20**, are observed in 58 and 10% yield, respectively.

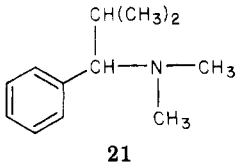


19



20

The products reported by Jones and Hauser[8] from reaction of the isopropylbenzyldimethylammonium iodide (**1**) were at variance with our observations, so we reinvestigated this reaction. Although Jones and Hauser claimed that two Sommelet–Hauser products were obtained, only one (**2**) was independently synthesized. The second (**3**) was inferred from VPC and by analogy to other compounds in which R was a primary group. The Sommelet–Hauser product **3** would require the intermediacy of a tertiary type A ylide. From our generalizations, it seemed likely that a benzylic type C ylide would give rise to a Stevens rearrangement involving a secondary isopropyl radical. Repetition of the experiment revealed that, in addition to an elimination product, one Sommelet–Hauser product (**2**) and one Stevens product (**21**) were indeed



21

formed. Small quantities of dimer **16** were also obtained. The identity of **21** was confirmed by independent synthesis and enhancement of the VPC signal with an authentic sample.

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were determined with a Beckman Acculab 1 or a Perkin-Elmer Model 521 instrument. Proton NMR spectra were obtained on a Varian HA 100 NMR spectrometer in $CDCl_3$ or acetone-d_6 with Me_4Si as the internal standard.

Either a Varian Aerograph Model 90-P or an Aerograph Model A-700 gas chromatographic instrument was used with a 20% Carbowax 20 M on 45/60 mesh Chromosorb W column. Thermal conductivity detectors were employed and helium was the carrier gas.

Materials. Isopropylbenzyldimethylammonium iodide was prepared according to the directions of Jones and Hauser;[8] mp 192–194 °C dec (lit.[8] 119–121 °C). The quaternary bromides were prepared in the following manner. The appropriate primary amine was dimethylated by using formic acid and formaldehyde.[21] The resulting tertiary amine was then refluxed overnight with an equimolar amount of benzyl bromide in dry benzene. Satisfactory analyses were obtained for each salt. The following melting points were obtained: **6**, 148 °C, **7**, 190–192 °C (lit.[22] 194–196 °C); **8**, 204–206 °C; **9**, 185–188 °C (lit.[14] 184–186 °C); **10**, 205–207 °C; **14**, 168 °C.

Table II. Conditions for the Base Reaction

	mol of metal	mol of salt	volume of NH_3, mL	% reacn	time, h
1a	0.098	0.070	100	67	1.7
1b	0.060	0.042	100	36	1.7
1c	0.11	0.068	250	20	2
1d	0.11	0.068	250	74	2
5	0.16	0.12	200	81	4
6	0.098	0.070	100	69	1.7
7a	0.098	0.070	100	57	1.7
7b	0.10	0.060	200	73	4
8	0.098	0.070	100	69	1.7
9	0.098	0.060	100	55	1.7
10	0.20	0.10	200	95	5
11	0.10	0.067	200	81	8
13	0.16	0.11	200	88	4
14	0.019	0.019	200	79	2
15	0.18	0.048	200	98	2.5

Preparation of Cyclobutylcarbinylbenzyldimethylammonium Chloride (13). *N,N*-dimethylcyclobutylcarboxamide, bp 75 °C (0.9 mm), was obtained in 84% yield by successive treatment of 60 g (0.6 mol) of cyclobutanecarboxylic acid with thionyl chloride and dimethylamine. The amide was then treated with a little excess fresh lithium aluminum hydride in dry ether. Sodium hydroxide (10%) was then added dropwise to the reaction mixture in an ice bath. The amine was extracted with ether and dried over $MgSO_4$. To this ethereal solution an excess of benzyl chloride was added and the resulting solution was allowed to stand overnight. A white precipitate (**13**), mp 189 °C dec, was obtained in 55% yield: NMR δ 7.40–7.80 (m, 5 H), 5.12 (s, 2 H), 3.75 (d, 2 H), 3.23 (s, 6 H), 1.5–3.0 (m, 7 H).

Anal. Calcd for $C_{14}H_{22}NCl$: C, 70.00; H, 9.16; N, 5.83. Found: C, 69.88; H, 9.12; N, 5.80.

Preparation of (Ethyl-β-d_3)benzyldimethylammonium Iodide (11). A solution of 15.5 g of *N*-methylbenzylamine (0.128 mol) in 25 mL of dry benzene was added to a solution of acetyl-β-d_3 chloride (10 mL, 0.125 mol) and 5 mL of pyridine in 25 mL of dry benzene. The benzene solution was washed with acid and with base and dried over $MgSO_4$. Evaporation of the solvent left 16.0 g of amide (68% yield). The crude amide was dissolved in 80 mL of dry ether and treated with 3.5 g of lithium aluminum hydride. A 90% yield of (ethyl-β-d_3)benzylmethylamine, bp 106 °C (50 mm), was obtained. The amine was treated with excess methyl iodide in ether at room temperature to give salt **11**, mp 118 °C dec, in 94% yield: NMR δ 3.20 (s, 6 H), 3.69 (s, 2 H), 4.97 (s, 2 H), 7.30–7.56 (m, 3 H), 7.64–7.84 (m, 2 H).

Anal. Calcd for $C_{11}H_{18}NI$: C, 44.84; H, 6.15; N, 4.69; I, 43.28. Found: C, 44.89; H, 6.13; N, 4.76; I, 43.20.

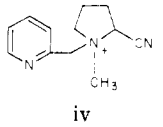
Preparation of Cyclobutylbenzyldimethylammonium Iodide (5). Cyclobutylbenzylamine[23] was converted to cyclobutylbenzylmethylamine, bp 70 °C (0.9 torr), in 94% yield by using the Eschweiler–Clark[21] procedure.

The amine was treated with excess methyl iodide in ether at room temperature to produce **5**, mp 155 °C dec, in 90% yield: NMR δ 1.55–2.7 (m, 6 H), 3.10 (s, 6 H), 4.53 (qn, 1 H), 4.78 (s, 2 H), 7.4–7.5 (m, 3 H), and 7.7–8.0 (m, 2 H).

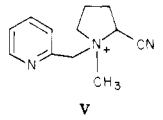
Anal. Calcd for $C_{13}H_{20}NI$: C, 49.21; H, 6.31; N, 4.41; I, 40.06. Found: C, 49.04; H, 6.09; N, 4.16; I, 39.69.

Preparation of *cis*-(2-Phenylcyclopropyl)benzyldimethylammonium Iodide (15). *cis*-(2-Phenylcyclopropyl)-benzylamine was prepared from *cis*-2-phenylcyclopropylamine[24] and benzaldehyde in the same manner as cyclobutylbenzylamine.[23]

(20) E. B. Sanders, H. V. Secor, and J. I. Seeman, *J. Org. Chem.*, 43, 324 (1978), report the Sommelet–Hauser reaction of salt iv via a tertiary ylide v. Resonance stabilization by the cyano group allows this tertiary ylide to form.



iv



v

(21) R. N. Icke, B. B. Wisegarner, and G. A. Alles, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 723.

(22) K. Nagarajan, C. L. Kulkarni, and R. K. Shah, *Indian J. Chem.*, 9, 748 (1971).

(23) C. L. Bumgardner, E. L. Lawton, and J. G. Carver, *J. Org. Chem.*, 37, 407 (1972).

(24) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, 70, 2198 (1948).

A methanolic solution of the amine was refluxed with excess methyl iodide for 8 h to produce the quaternary salt in 72% yield: mp 156 °C dec; NMR δ 1.48 (m, 1 H, J = 24 Hz), 1.91 (m, 1 H, J = 20 HZ), 2.70 (m, 1 H, J = 24 Hz), 2.84 (s, 3 H), 3.08 (s, 3 H), 3.97 (m, 1 H, J = 22 Hz), 5.10 (s, 2 H), 7.30 (s, 5 H), 7.44–7.75 (m, 5 H).

Anal. Calcd for $C_{18}H_{22}NI$: C, 56.99; H, 5.80; N, 3.69; I, 33.51. Found: C, 56.87; H, 5.76; N, 3.60; I, 33.10.

Typical Procedure for the Reaction of the Quaternary Salts with Alkali Amide. Ammonia was condensed into a round-bottom, three-necked flask, which was fitted with a dry ice condenser filled with a dry ice–acetone slush. To the ammonia was added freshly cut metal. A small amount of ferric nitrate was added and the color of the liquid changed from blue to gray-black. The quaternary ammonium salt was added in small portions by means of a solid addition funnel. The reaction mixture was then stirred for a period of time. Excess amide was decomposed by the slow addition of 5 g of ammonium chloride, and ether was then added. The dry ice condenser was replaced by a water condenser, and the ammonia was allowed to evaporate overnight.

After the ammonia had evaporated, water was added and the resulting layers were separated. The aqueous layer was washed with ether. The combined ether solutions were extracted with two 50-mL portions of 10% hydrochloric acid. The combined acid extracts were made strongly alkaline with 10% sodium hydroxide, and the oil which separated was extracted with ether. The ether extract was washed with water and dried over magnesium sulfate.

After the drying agent was removed by filtration, the ether was evaporated and the crude basic fraction was weighed. The moles of metal and salt, volume of solvent, reaction time, and yield for each salt are shown in Table II.

The crude basic fraction was distilled through a small Vigreaux column to separate the benzyldimethylamine. The higher boiling isomeric tertiary amines were examined by NMR and subjected to VPC; retention times were compared with those for known samples. In the case of the *tert*-butyl salt, the reaction mixture was filtered before it was distilled. The white solid obtained was recrystallized from benzene: mp 194 °C dec (lit.[25] 196.5 °C); NMR δ 1.96 (s, 12 H), 4.10 (s, 2 H), 7.20–7.46 (m, 10 H).

Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.59; H, 8.96; N, 10.44. Found: C, 80.75; H, 9.13; N, 10.35.

A neutral fraction, also obtained from the reaction of the *tert*-butyl salt, contained trace quantities of *tert*-butyl alcohol and benzaldehyde.

The physical properties of the neutral elimination product from **14** and **15** as determined by TLC, NMR, the mass spectrum, and the glass temperature were identical. Spectral information suggests that the neutral material is poly(phenylcyclopropene): NMR ($CDCl_3$) δ 0.6–1.4, 1.4–2.1, 2.1–2.8 (distorted m, 3 H), 6.8–7.8 (distorted m, 5 H); mass spectrum m/e 465 (M^+ – 115), 373, 360, 348, 115, 91.

Products of Reaction of 7 with Amide. Cyclohexyl(*o*-methylbenzyl)methylamine was prepared by refluxing 0.01 mol of *N*-methylcyclohexylamine with 0.01 mol of α-bromo-*o*-xylene in absolute ethanol for 2 h. After extraction with acid and base, the product was obtained in 42% yield: bp 122–4 °C (0.8 mm); NMR δ 2.14 (s, 3 H), 2.35 (s, 3 H), 3.5 (s, 2 H), 7.1 (m, 4 H).

Anal. Calcd for $C_{15}H_{23}N$: C, 82.94; H, 10.59; N, 6.45. Found: C, 82.85; H, 10.55; N, 6.53.

This amine enhanced the second VPC signal from the mixture of higher boiling amines obtained from treatment of **7** with amide ion.

Cyclohexyl phenyl ketone oxime[26] (0.036 mol) was treated with 0.126 mol of lithium aluminum hydride in ether for 7 h. After extraction with acid and base, (α-cyclohexylbenzyl)amine was isolated in 78% yield, bp 110 °C. This primary amine was methylated by using the Clark–Eschweiler procedure[21] to form *N*,*N*-dimethyl(α-cyclohexylbenzyl)amine in 21% yield: bp 130–5 °C (8 mm); NMR δ 2.10 (s, 6 H), 1–2 (m, 11 H), 3.01 (d, 1 H), 7–7.6 (m, 5 H).

Anal. Calcd for $C_{15}H_{23}N$: C, 82.94; H, 10.59; N, 6.45. Found: C, 82.60; H, 10.85; N, 6.53.

This amine enhanced the first VPC signal from the mixture of higher boiling amines obtained from treatment of **7** with amide ion.

The ratio of rearrangement products from **1**, **6**–**11**, and **13** was based on the relative integrals of the benzylic protons. A doublet, corresponding to one proton, was observed for the Stevens products, and further downfield a singlet corresponding to two protons in the Sommelet–Hauser products was observed.

Deuterated Benzyldimethylamine. The benzyldimethylamine obtained from the reaction of **11** with amide ion was methylated with methyl iodide. The quaternary salt, mp 178 °C (lit.[6] 178 °C), was ionized at 14 eV in an AEI-MS12 mass spectrometer. Peaks at m/e 92 (100) and at m/e 91 (9.88) were obtained. A sample of pure benzyltrimethylammonium iodide gave a peak at m/e 91 (100) and no peak at m/e 90. Consequently, 91% of the salt contained one deuterium. The NMR spectrum of the deuterated salt, in D_2O, was consistent: δ 3.54 (s, 9 H), 5.95 (s, 1 H), 8.03 (s, 5 H).

Independent Synthesis of (α-Isopropylbenzyl)dimethylamine (24). 1-Phenyl-2-methylpropylamine was prepared from isobutyrophenone by the Leuckart reaction.[27] The primary amine was dimethylated in the conventional manner[21] to give (α-isopropylbenzyl)dimethylamine: bp 107 °C (19 mm); n_D^{28} 1.4985 (lit.[24] bp 56–7 °C (0.5 mm), n_D^{23} 1.4998); NMR δ 7.2 (m, 5 H), 2.84 (d, 1 H), 2.28 (m, partly obscured), 2.14 (s), 1.92 (q, 6 H). Signals at δ 2.14 and 2.28 equal seven hydrogens. The VPC signal of the amine product mixture from **1c** was enhanced by the addition of **24**. The relative amounts of Sommelet–Hauser and Stevens products were also determined by VPC.

Registry No. **1**, 27701-34-4; **1a**, 70160-71-3; **2**, 70160-72-4; **4**, 14213-78-6; **5**, 70160-73-5; **6**, 70160-74-6; **7a**, 34173-54-1; **8**, 70160-75-7; **9**, 70160-76-8; **10**, 70160-77-9; **11**, 70160-78-0; **12**, 70160-79-1; **13**, 70160-80-4; **14**, 70160-81-5; **15**, 70160-82-6; **16**, 61900-97-8; **17**, 70160-83-7; **18**, 70160-84-8; **19**, 70160-85-9; **20**, 70160-86-0; **21**, 70160-87-1; cyclopropyldimethylamine, 58862-94-5; cyclopentyldimethylamine, 18636-91-4; cyclohexyldimethylamine, 98-94-2; cycloheptyldimethylamine, 18636-92-5; cyclooctyldimethylamine, 17630-21-6; *tert*-butyldimethylamine, 918-02-5; cyclopropylcarbinyldimethylamine, 58862-95-6; *trans*-2-phenylcyclopropyldimethylamide, 59192-94-8; benzyl bromide, 100-39-0; *N*,*N*-dimethylcyclobutylcarboxamide, 57056-80-1; cyclobutanecarboxylic acid, 3721-95-7; isopropyldimethylamine, 996-35-0; benzyl chloride, 100-44-7; *N*-methylbenzylamine, 103-67-3; *N*-benzyl-*N*-methyl-d_3-acetamide, 70160-88-2; ethyl-β-d_3-benzylmethylamine, 70160-89-3; cyclobutylbenzylamine, 32861-52-2; cyclobutylbenzylmethylamine, 70160-90-6; *cis*-2-(phenylcyclopropyl)benzylamine, 39933-77-2; *cis*-2-phenylcyclopropylamine, 13531-35-6; poly(phenylcyclopropene), 70161-08-9; cyclohexyl(*o*-methylbenzyl)methylamine, 70160-91-7; *N*-methylcyclohexylamine, 100-60-7; α-bromo-*o*-xylene, 89-92-9; cyclohexyl phenyl ketone oxime, 1136-58-9; (α-cyclohexylbenzyl)amine, 23459-35-0; *N*,*N*-dimethyl(α-cyclohexylbenzyl)amine, 69903-32-8; benzyl(trimethyl-d_1)ammonium iodide, 70160-92-8; 1-phenyl-2-methylpropylamine, 6668-27-5; isobutyrophenone, 611-70-1; (α-isopropylbenzyl)dimethylamine, 70160-87-1; 1-propene, 115-07-1; phenethylisopropylmethylamine, 70160-93-9; cyclopropene, 2781-85-3; *o*-methylbenzylcyclopropylmethylamine, 14213-79-7; *o*-methylbenzylcyclobutylmethylamine, 70160-94-0; cyclobutene, 822-35-5; cyclopentene, 142-29-0; *o*-methylbenzylcyclopentylmethylamine, 70160-95-1; phenethylcyclopentylmethylamine, 70160-96-2; cyclohexene, 110-83-8; phenethylcyclohexylmethylamine, 70160-97-3; cycloheptene, 628-92-2; *o*-methylbenzylcycloheptylmethylamine, 70160-98-4; phenethylcycloheptylmethylamine, 70160-99-5; *cis*-cyclooctene, 931-87-3; *o*-methylbenzylcyclooctylmethylamine, 70161-00-1; phenethylcyclooctylmethylamine, 70161-01-2; 2-methylpropene, 115-11-7; *o*-methylbenzyl-*tert*-butylmethylamine, 70161-02-3; phenethyl-*tert*-butylmethylamine, 70161-03-4; 1,1-dideuteroethene, 6755-54-0; *o*-methylbenzyl(cyclopropylmethyl)-methylamine, 70161-04-5; α-cyclopropyl-*o*-methylbenzyldimethylamine, 70161-05-6; phenethyl(cyclopropylmethyl)methylamine, 70161-06-7; methylenecyclobutane, 1120-56-5.

(25) Y. A. Ustynyuk and E. G. Perevalora, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 62 (1964); *Chem. Abstr.*, **60**, 9310e (1964).
(26) W. Scharvin, *Chem. Ber.*, **30**, 2864 (1897).
(27) A. W. Ingersoll, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 503.
(28) J. Ficini and H. Normant, *Bull. Soc. Chim. Fr.*, 1454 (1957).