[Chem. Pharm. Bull. 32(5)1770—1779(1984)]

Amino-Claisen Rearrangement. IV.[1] Quaternary Amino-Claisen Rearrangement of *N*-Allyljulolidinium Derivatives[2]

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(Received September 7, 1983)

The amino-Claisen rearrangements of 9-unsubstituted and 9-substituted *N*-allyljulolidinium halides were investigated. The former compounds can be regarded as aniline derivatives in which the two *ortho* sites are occupied. In the latter compounds, the two *ortho* positions and the *para* position are all blocked. *N*-Allyljulolidinium halides rearranged into 9-allyljulolidine. However, 9-substituted *N*-allyljulolidinium halides gave 8-allyl-9-substituted julolidines. This *meta* rearrangement constitutes the first reported example of *meta* amino-Claisen rearrangement. The reaction pathways can be rationalized in terms of a combination of [3,3] and [1,2] sigmatropic rearrangements.

Keywords——amino-Claisen rearrangement; *meta*-rearrangement; *N*-allyljulolidinium halide; 9-substituted-*N*-allyljulolidinium halide; 9-allyljulolidine; 8-allyl-9-substituted julolidine; [3,3] sigmatropic rearrangement; [1,2] sigmatropic rearrangement

In the course of our studies on amino (N)-Claisen rearrangement[3] we were interested in the quaternary N-Claisen rearrangement of julolidinium derivatives in which the *ortho* and *para* positions of the aniline framework are all occupied by substituents. As the first steps, we investigated the rearrangement of *N*-allyljulolidinium halides and observed *para* rearrangement of the allyl group. We next studied the N-Claisen rearrangement of 9-substituted *N*-allyljulolidinium derivatives and found a novel *meta* migration of the allylic moiety. This finding constitutes the first reported example of *meta* N-Claisen rearrangement.

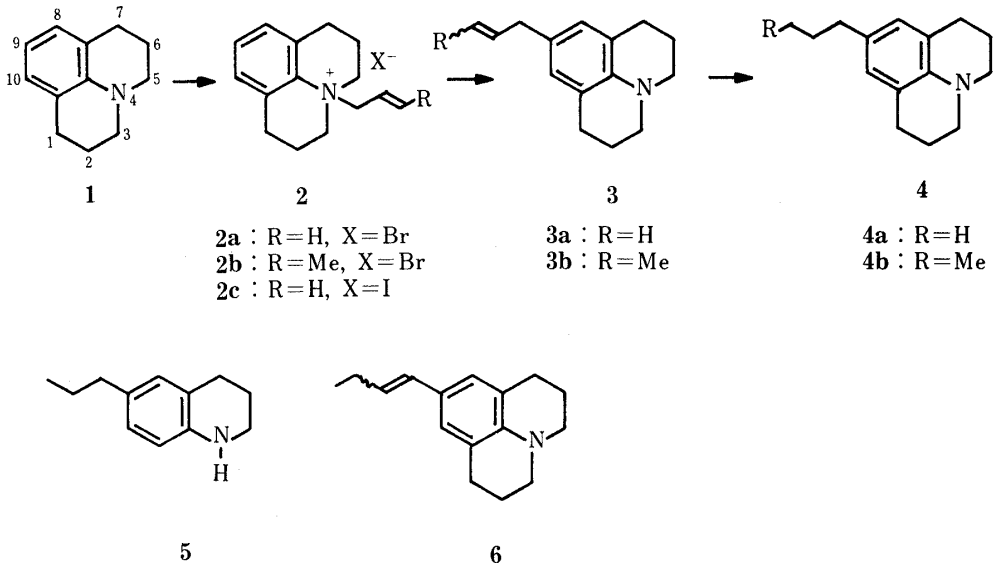
1. N-Claisen Rearrangement of *N*-Allyljulolidinium Halides (2)

The title compounds **2** were prepared according to the usual method, *i.e.*, the reaction of julolidine **1** with allyl halides. The isolation of **2** required careful work-up and crystallization. The yields were generally poor (Table III).

The rearrangement of **2** was conducted under two reaction conditions, A and B. In general the weakly basic reaction condition B gives a better result than condition A.[3] The allylic moiety can migrate from quaternary nitrogen to the *para* position in good yields. Deallylation is the only side reaction (Table I). The product **3a** was catalytically hydrogenated to **4a** and identified by comparison with an authentic specimen derived from **5**.[3b] The product **3b** was a mixture of geometrical isomers ($E:Z=57:36$), *vide infra*, and they could not be separated. This mixture **3b** was reduced to **4b**, which was identical with an authentic specimen prepared by the hydrogenation of **6** (obtained by the Wittig reaction[5] of 9-formyljulolidine[6]).

2. N-Claisen Rearrangement of 9-Substituted *N*-Allyljulolidinium Halides (8)

The compounds **8** were prepared by the usual method in good yields (Table III). The starting materials **7a** and **7d** were prepared from *p*-anisidine and *p*-toluidine respectively.[4a] The phenol **7b** was obtained as a by-product in the preparation of **7a** from 6-methoxy-1,2,3,4-tetrahydroquinoline and 1,3-bromochloropropane.[4b] This compound was transformed into **7c** by a usual method. The 9-bromojulolidine **7e** was readily colored and labile if prepared



1 2 3 4

2a : R=H, X=Br
2b : R=Me, X=Br
2c : R=H, X=I

3a : R=H
3b : R=Me

4a : R=H
4b : R=Me

5 6

Chart 1

according to the literature[7] but was relatively stable when prepared by the bromination of **1** with *N*-bromosuccimide (NBS) in dimethylformamide (DMF).[8] The salts **8** were purified by recrystallization, but **8e** was isolated from the reaction mixture by column chromatography as an amorphous solid.

The rearrangement results are summarized in Table I. The reaction products were analyzed by gas liquid chromatography (GLC) and separated by flash column chromatography.[9] The structures of **9** were deduced from their mass and nuclear magnetic resonance spectra (MS and NMR), which provided the molecular weight (M^+) and functional groups (allyl group and a single aromatic proton). The products **9a**, **9b** and **9c** were cyclized into the single compound **11** by acid catalysis, and thus the site of the allyl moiety of these compounds was proved. Following these observations, the structure of **9d** was assigned. The structures of the minor products **10** obtained from **8a** and **8c** under reaction condition A were similarly deduced from their mass (M^+) and NMR (two allyl groups and no aromatic proton) spectra.

3. N-Claisen Rearrangement of *N*-Crotyl-9-methoxyjulolidinium Bromide (12)

In order to obtain information about the mechanism of the *meta* rearrangement, **12** was rearranged and the products were analyzed by GLC and gas chromatography-mass spectrometry (GC-MS) (Table II). The products **7a** and **3b** were isolated from the reaction mixture by column chromatography and identified by comparison with authentic specimens prepared previously. The product **3b** was a mixture of the geometrical isomers (*E*:*Z*=4:5). The tentative assignments of these isomers are based upon their retention times (t_R) on GLC in comparison with those of the isomers *E*-**14** and *Z*-**14**, *vide infra*. A mixture of **13** and **14** was preparatively separated by GLC and small amounts of pure specimens were obtained. The presence of the isobutenyl group and a single aromatic proton supports the structure of **13**. The product **14** was separated into two isomers *E*-**14** and *Z*-**14** and these isomers were catalytically hydrogenated to yield a single compound, **16**. In the NMR spectrum the isomer *Z*-**14** shows methyl signals at δ 1.77 as a doublet, J=5 Hz, while *E*-**14** has a multiplet at δ 1.63. These characteristic patterns of methyl signals are in good agreement with the configurational assignments. The GC-MS analyses of the hydrogenated products also support these structures. The product **15** shows *m/z*: 244 ($M^+-15-29$), which corresponds to the loss of methyl of a methoxy group and an ethyl group from M^+. The product **16** has a peak at *m/z*: 202 ($M^+-15-42$) owing to the loss of methyl of a methoxy and a propyl group with

TABLE I. Products Formed from **2a—c** and **8a—f**

Substrate	React. cond.[a]	Crude yield (%)	Products (%)[b]			
			meta	*para*	Deallyl.	Others
2a	A	78.8	—	**3a**: 97.8	**1**: 1.5	
	B	92.8	—	**3a**: 87.3	**1**: 11.3	
2b	B	89.0	—	**3b**: 93.0	**1**: 7.0	
2c	B	93.3	—	**3a**: 80.9	**1**: 18.4	
8a	A	84.5	**9a**: 82.1	**3a**: <1	**7a**: 12.6	**10a**: 3.9
	B	82.7	**9a**: 32.0	**3a**: 50.4	**7a**: 17.5	
8b	A	96	**9b**: 53*			
8c	A	85	**9c**: 85.6	**3a**: <1	**7c**: 8.7	**10c**: 5.3
	B	77	**9c**: 35.3	**3a**: 54.6	**7c**: 9.9	
8d	B	63	**9d**: 67	—	**7d**: 32	
8e	A	67		**3a**: 92.2	**7e**: 3.9	
	B	57		**3a**: 87.7	**7e**: 10.0	
8f	B	84	**9f**: 31.9	**3a**: 32.7	**7a**: 34.6	

a) Reaction conditions: A solution of the substrate (2 mmol) in glycerol–water (2:1) was heated at 140 °C (bath temperature) for 2—4 h in the absence (A) or in the presence (B) of sodium hydrogen carbonate (2 mmol).
b) Yields are based on GLC analyses. The yield with an asterisk * is the isolated yield.

TABLE II. Products Formed from **12**

Substrate	React. cond.	Crude yield (%)	Products (%)					
			7a	*E*-**3b**	*Z*-**3b**	**13**	*E*-**14**	*Z*-**14**
12	A/4h	84.6	35	0.1	0.3	12	39	12
12	B	86.0	40	1.6	2.2	14.1	34	8

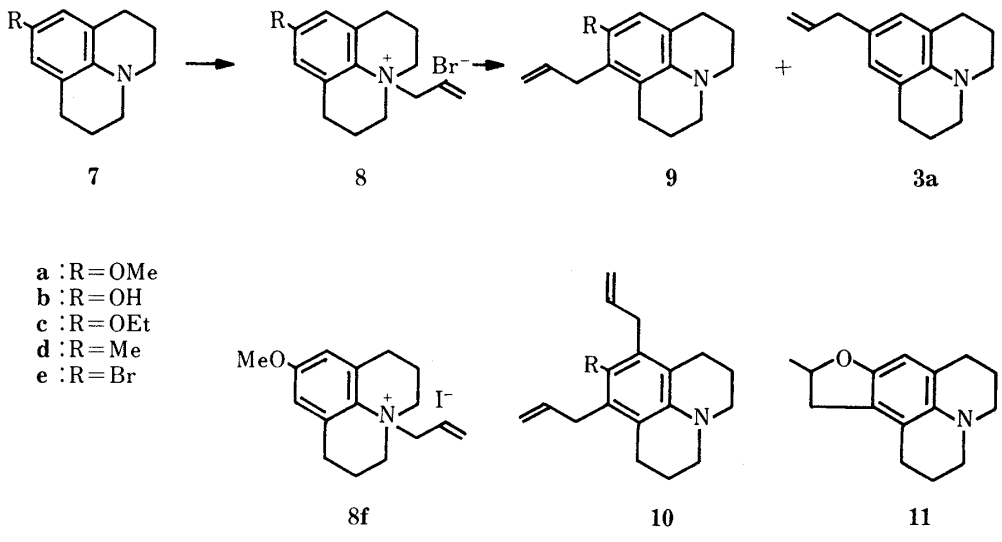


Chart 2

hydrogen migration from M^+.

4. Rearrangement Mechanism

The N-Claisen rearrangements described above can be rationalized in terms of sigma-

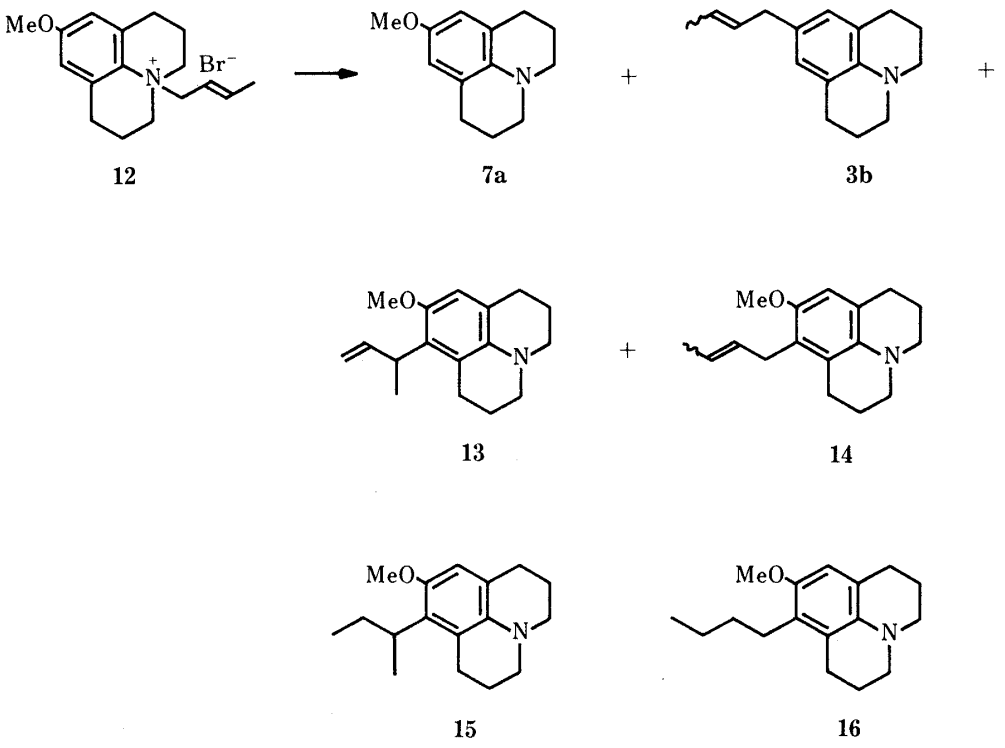


Chart 3

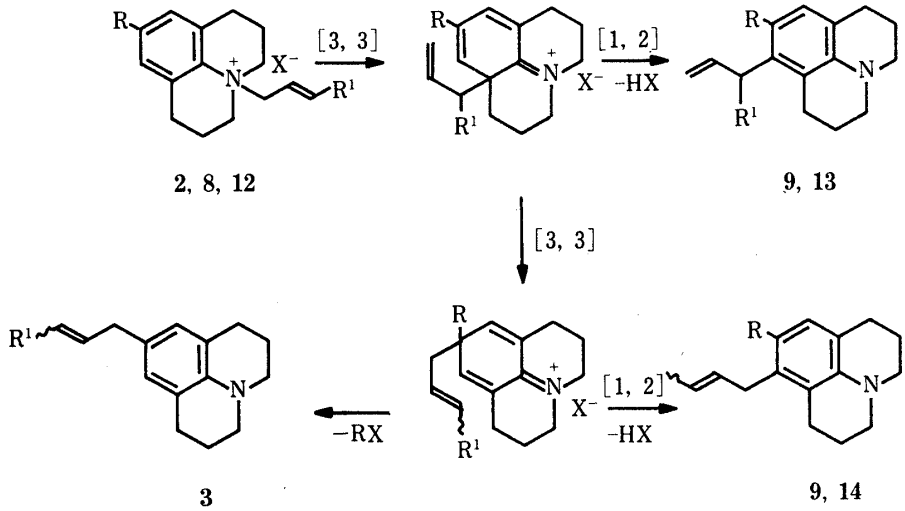


Chart 4

tropic mechanisms. The rearrangement of 2 *via* two [3,3] sigmatropic pathways gives **3**. The absence of any product with an isomeric side chain such as an isobutenyl group in the reaction products excludes the dissociation-recombination mechanism. Since the product **3b** was a mixture of geometrical isomers ($E:Z=57:36$), a portion of the transition states must involve boat conformation during the rearrangement.[1,10]

There are two pathways for *meta* rearrangement. The reaction of **12** allowed all possible products (Chart 4). The replacement of 9-substituents became the major pathway in the reactions of **8a**, **8c**, and **8f** under basic condition B and in that of **8e** under both reaction conditions. No replacement was possible in **8d**. The formation of **3a** from **8** suggests that the

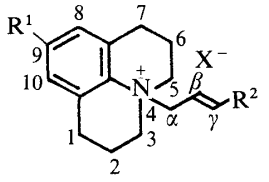
allyl groups migrate to the *para* position intramolecularly during the reaction. The product **13** is derivable *via* [3,3] and [1,2] sigmatropic rearrangements. The formation of **14** supports the presence of the pathway *via* two [3,3] rearrangements and one [1,2] rearrangement. The presence of the two pathways for **13** and **14** can also account for the fromation of **9**. Since no change of the products pattern was observed in the reaction of **8a** under condition B in the presence of the radical scavenger, 4,4′-thiobis(6-*tert*-butyl-*m*-cresol), the involvement of a radical intermediate in the reaction is unlikely. The possibility of intermolecular reaction was checked by trying a crossover reaction. When an equimolar mixture of **8f** and **1** was subjected to reaction condition A, the conversion of **8f** into **9a** was more than 80% and the recovery of **1** was 96%. The formation of **3a**, the displacement as well as crossover reaction product, was less than 2%. The crossover reaction between **8c** and **12** was also investigated. The products were analyzed in detail by GLC and GC-MS measurements (see Experimental). No product due to crossover migration of the crotyl group was detected. The product derived from crossover migration of the allyl group under reaction condition B was not observed, but in the reaction product obtained under condition A, about 2.5% of the product derived by crossover migration of the allyl group was detected. The difference presumably reflects the fact that the abstraction of a proton from the rearrangement intermediate is faster under basic condition B than under acidic condition A, so reaction condition A provides more opportunity for a crossover reaction to occur than condition B. Since the above two crossover reactions rule out the intermolecular mechanism as the major course of reaction, the quaternary N-Claisen rearrangement may be concluded to proceed *via* a sigmatropic mechanism as shown in Chart 4. The product **10** was formed only under condition A. As described above, the abstraction of a proton is slow under condition A, so the product **9** may suffer some transfer of the allyl group onto the nitrogen atom from **8** or the reaction intermediates. Subsequent migration of

TABLE III. Physicochemical Data

Compound	Yield (%)	Dec. (°C) (solvent)[b]	IR ν_{max}^{KBr} cm^{-1}	Analysis (%)	Calcd (Found)			
					C	H	N	X
2a	27	147.5—149 (C–A)	3060, 2855, 795	$C_{15}H_{20}BrN$	61.23 (60.95	6.85 6.96	4.76 4.65	27.16 27.27)
2b	25.3	145—148 (D–A)	1665, 990, 940, 800, 785	$C_{16}H_{22}BrN$	62.34 (62.13	7.19 7.57	4.54 4.40	25.92 25.64)
2c	12.2	140.5—141 (C–A)	1605, 1462, 945, 800, 785, 755	$C_{15}H_{20}IN$	52.80 (53.08	5.91 6.14	4.10 3.88	37.19 36.99)
8a	64	155—156.5 (C–A)	2840, 1600, 1295, 1160, 928, 770	$C_{16}H_{22}BrNO$	59.26 (59.14	6.84 7.13	4.32 4.32	24.64 24.61)
8b	70.4	174—175 (M–A)	3350, 1598, 1175, 782	$C_{15}H_{20}BrNO$	58.07 (58.31	6.50 6.45	4.52 4.47	25.76 26.03)
8c	75	166—169 (D–A)	1602, 998, 780	$C_{16}H_{22}BrN$	62.34 (62.11	7.19 7.09	4.54 4.26	25.92 26.10)
8d	69.2	136—137 (D–A)	1595, 1175, 1042, 770	$C_{17}H_{24}BrNO$	60.36 (60.45	7.15 7.27	4.14 4.17	23.62 23.45)
8e	23.6	115—119[a]	1572, 1467, 928, 762	$C_{15}H_{19}Br_2N$				42.83 (42.61)
8f	81	161—162 (D–A)	1610, 1598, 1493, 1300, 1193, 1178, 790	$C_{16}H_{22}INO$	51.76 (51.81	5.97 6.18	3.77 3.55	34.18 34.20)
12	86	155—158 (D–A–E)	1667, 1170, 1050, 775	$C_{17}H_{24}BrNO$	60.36 (60.08	7.15 7.28	4.14 4.12	23.62 23.49)

a) In a sealed tube.
b) C, chloroform; A, acetone; M, methanol; D, dichloromethane; E, ethanol.

TABLE IV. ^{1}H-NMR Data



Substrate	C-1-H C-7-H	C-2-H C-6-H	C-3-H C-5-H	Ar-H [2H]	α-H [2H]	β-H [1H]	γ-H [2H]	Other signals	
2a	3.25 t, J=7	2.44 m	3.5—4.4 m	7.0—7.5 m	4.37 d, J=5.5		5.6—6.3 m		
2b	3.20 t, J=7	2.43 m	3.93 m	7.23 m	4.20 d, J=7	5.73 td, J=7, 15	6.40 qd, J=6, 15	1.87 3H, d, J=6	
2c	3.27 t, J=7	2.43 m	3.5—4.2 m	7.1—7.5 m	4.37 d, J=5.5		5.7—6.2 m		
8a	3.17 t, J=7	2.43 m	3.5—4.3 m	6.63 s	4.30 d, J=5.5		5.6—6.1 m	3.80 3H, s	
8b	3.07 t, J=6	2.27 m	3.5—4.1 m	6.63 s	4.30 d, J=6		5.6—6.1 m		
8c	3.17 t, J=7	2.43 m	3.5—4.4 m	6.93 s	4.30 d, J=6		5.6—6.2 m	2.32 3H, s	
8d	3.20 t, J=7	2.43 m	3.5—4.3 m	6.63 s	4.30 d, J=5.5		5.6—6.3 m	4.03 2H, q, J=7	1.40 t, J=7
8e	3.23 t, J=6	br	br	7.30 s	4.36 d, J=5		br		
8f	3.20 t, J=7	2.43 m	3.5—4.2 m	6.70 s	4.28 d, J=5.5		5.7—6.2 m	3.83 3H, s	
12	3.20 t, J=7	2.40 m	3.93 m	6.67 s	4.20 d, J=8	5.70 td, J=8, 16	6.40 qd, J=6, 16	1.90 3H, d, J=6	3.80 3H, s

the allyl group can then lead to the formation of **10**. This side reaction may be avoided by dilution of the reaction solution.

A tertiary nitrogen atom on an aromatic ring generally does not direct the functionalization of the aromatic ring except through a resonance effect. However, the quaternary N-Claisen rearrangement makes it possible to introduce allyl substituents onto the aromatic ring by the sigmatropic mechanism. Thus, this reaction may be useful as a new synthetic tool.

Experimental[11]

***N*-Allyljulolidinium Bromide (2a)**——A mixture of julolidine **1**[4b] (2.3 g) and allyl bromide (3.9 g) in acetonitrile (20 ml) containing two drops of DMF was left at room temperature (rt) for 5 months. The reaction mixture was evaporated and the residue was suspended in acetone for 5 d. The solid (1.954 g) was collected and recrystallized to give 0.844 g (21.6% yield) of **2a**. Similar work-up of the filtrates gave another crop of crystals (0.216 g; total 1.06 g, 27.1% yield).

***N*-Crotyljulolidinium Bromide (2b)**——A solution of julolidine **1** (2.0 g, 11.5 mmol) and crotyl bromide (10.0 g, 75 mmol; contained 15% of 3-bromo-1-butene) in acetone (50 ml) containing DMF (2 drops) and HMPA (3 drops) was left at rt for 2 weeks. The precipitates were collected and washed with acetone to give a red crystalline product (0.9 g, 25.3% yield). The crude product was purified by column chromatography under pressure on silica gel (230—400 mesh, 16.0 g). Elution with the lower layer of a mixture of chloroform, methanol and water (5 : 5 : 3) after shaking gave pure **2b** (660 mg).

***N*-Allyljulolidinium Iodide (2c)**——A solution of allyl iodide (3.5 g, 21 mmol) in dichloromethane (60 ml) was filtered through an alumina column (Al_2O_3 15 g) then added to julolidine **1** (3.2 g, 18.5 mmol). The resulting solution was refluxed in the presence of molecular sieves (3A, 1.5 g) for 53 h under a nitrogen atmosphere. Evaporation gave a darkbrown residue, which was washed with ether. The residual tar (3.62 g) was crystallized to give **2c** (0.77 g).

Typical Procedure for Rearrangement——A solution of **2** (2 mmol) in glycerol–water (2:1, 6—8 ml) in the absence (reaction condition A) or in the presence of sodium hydrogen carbonate (2 mmol) (reaction condition B) was heated at 140 °C (bath temperature) for 2 h. The reaction mixture was basified with sodium carbonate then extracted with ether three times to give the crude product, which was sufficiently pure, or was purified as described for each compounds.

9-Allyljulolidine (3a)——The crude product was purified *via* picrate or hydrobromide formation. Liquid. IR ν_{max}^{film} cm^{-1}: 3070, 2850, 1628, 1498, 1304, 905. NMR δ: 2.00 (4H, m, C-2-H+C-6-H), 2.80 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.19 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 3.26 (2H, d, J=6.5 Hz, C$\underline{H}_2$–CH=CH$_2$. Singlet on irradiation at δ 6.03), 4.9—5.3 (2H, m, CH$_2$–CH=C$\underline{H}_2$), 6.03 (1H, tdd, J=6.5, 9, 17 Hz, CH$_2$–C$\underline{H}$=CH$_2$. Double d, J=9, 17 Hz, on irradiation at δ 3.26), 6.70 (2H, s, Ar–H). Picrate, mp 130.5—133.0 °C (EtOH). *Anal.* Calcd for $C_{21}H_{22}N_4O_7$: C, 57.01; H, 5.01; N, 12.66%. Found: C, 56.88; H, 5.26; N, 12.43%. Hydrobromide, mp 186—188 °C. IR ν_{max}^{KBr} cm^{-1}: 2400, 1640, 1195, 1017, 930.

9-Crotyljulolidine (3b)——GC-MS *m/z*: 227 (M^+, P^+), 212, 198, 186, 184, 170, 100 (both isomers have an identical fragmentation pattern). IR ν_{max}^{film} cm^{-1}: 1660, 1617, 1310, 967, 675. NMR δ: 1.72 (3H, m, =CH–C$\underline{H}_3$. Two singlets at δ 1.70 and 1.72 when irradiated at δ 5.53), 1.97 (4H, m, C-2-H+C-6-H), 2.77 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.10 (4H, t, J=5 Hz, C-3-H+C-5-H), 3.20 (2H, d, J=5 Hz, C$\underline{H}_2$–CH=CH–CH$_3$. Singlet on irradiation at δ 5.53), 5.53 (2H, m, CH$_2$–C$\underline{H}$=C$\underline{H}$–CH$_3$), 6.60 (2H, s, Ar–H).

9-Propyljulolidine (4a)——Crude **3a** (121 mg) in ethanol (15 ml) was hydrogenated over 5% Pd-C (74 mg) under hydrogen. The crude product (106 mg) was purified on silica gel (2.0 g) with dichloromethane to give **4a** (94 mg), which was identical with an authentic specimen[3] by GLC, IR and NMR comparisons.

9-(1-Butenyl)-julolidine (6)——Sodium hydride dispersed in oil (50%, 0.34 g, 7 mmol) was washed with dry benzene and pentane successively. Dry dimethylsulfoxide (DMSO) (15 ml) was added to the sodium hydride over a period of 5 min, then the mixture was warmed at 80 °C for 0.5 h. The basic solution was cooled on ice, and a solution of propyltriphenylphosphonium bromide (2.1 g, 5.5 mmol) in dry DMSO (25 ml) was added over 15 min, then a solution of 9-formyljulolidine[6] (1.05 g, 5 mmol) in dry DMSO (25 ml) was added over a further 15 min. After 1 h at 60 °C, the reaction mixture was poured into ice-water (50 ml) and extracted with ether (5 × 10 ml). The crude product (1.977 g) was dissolved in hexane and insoluble materials were filtered off. The soluble part (1 g) was purified by flash column chromatography (silica gel 30.4 g, dichloromethane), giving **6** (477 mg, 42% yield) and 9-formyljulolidine (131 mg, 12.4% recovery). The product **6** was a mixture of geometrical isomers (E:Z=38:61) on GLC. Both isomers have identical fragmentation patterns in GC-MS. These isomers were separated by preparative GLC (20% SE-30, stainless steel column 5 mm × 1 m; He, 75 ml/min; 225 °C). *E*-**6**: Liquid. IR ν_{max}^{film} cm^{-1}: 1672, 1308, 896, 715. NMR δ: 1.06 (3H, t, J=7 Hz, CH$_2$–C$\underline{H}_3$), 1.93 (4H, m, C-2-H+C-6-H), 2.37 (2H, quintet, J=7 Hz, CH=CH–C$\underline{H}_2$–Me), 2.79 (4H, t, J=6 Hz, C-1-H+C-7-H), 3.12 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 5.37 (1H, td, J=7, 11 Hz, Ar–CH=C$\underline{H}$–Et. Doublet, J=11 Hz on irradiation at δ 2.37), 6.16 (1H, d, J=11 Hz, Ar–C$\underline{H}$=CH–Et), 6.76 (2H, s, Ar–H). *E*-**6**: Liquid. IR ν_{max}^{film} cm^{-1}: 1678, 1311, 964. NMR δ: 1.08 (3H, t, J=7 Hz, CH$_2$–C$\underline{H}_3$), 1.93 (4H, m, C-2-H+C-6-H), 2.13 (2H, m, CH=CH–C$\underline{H}_2$–Me), 2.74 (4H, t, J=6 Hz, C-1-H+C-7-H), 3.13 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 6.00 (1H, td, J=6, 16 Hz, Ar–CH=C$\underline{H}$–Et. Doublet, J=16 Hz on irradiation at δ 2.13), 6.20 (1H, d, J=16 Hz, Ar–C$\underline{H}$=CH–Et), 6.84 (2H, s, Ar–H).

9-*n*-Butyljulolidine (4b)——a) The product **3b** (60 mg) was hydrogenated first over 5% Pd-C (20 mg) then over Adams catalyst (21 mg) in ethyl acetate (10 ml) under hydrogen, giving **4b** (55 mg). b) The mixture **6** (202 mg) was similarly reduced to give 183 mg of **4b** as a brown liquid. MS *m/z*: 229 (M^+), 186 (P^+). IR ν_{max}^{film} cm^{-1}: 1615, 1500, 1305, 885, 858. NMR δ: 0.92 (3H, t, J=7 Hz, CH$_2$–C$\underline{H}_3$), 1.47 (4H, m, CH$_2$–C$\underline{H}_2$–C$\underline{H}_2$–Me), 1.97 (4H, m, C-2-H+C-6-H), 2.46 (2H, t, J=7 Hz, Ar–C$\underline{H}_2$–Pr), 2.77 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.10 (4H, t, J=6 Hz, C-3-H+C-5-H), 6.63 (2H, s, Ar–H). Hydrochloride, mp 137—140 °C (dec.). IR ν_{max}^{KBr} cm^{-1}: 2100—2400, 1020, 864. NMR δ: 0.89 (3H, t, J=7 Hz, CH$_2$–C$\underline{H}_3$), 1.43 (4H, m, Ar–CH$_2$–C$\underline{H}_2$–CH$_2$–Me), 2.50 (6H, m, C-2-H+C-6-H+Ar–CH$_2$–Pr), 2.90 (4H, br s, C-1-H+C-7-H. Triplet, J=6 Hz, upon addition of deuterium oxide), 6.66 (2H, s, Ar–H). *Anal.* Calcd for $C_{16}H_{24}ClN \cdot 1/2H_2O$: C, 69.92; H, 9.17; Cl, 12.90; N, 5.10%. Found: C, 69.57; H, 8.91; Cl, 12.94; N, 5.06%.

9-Substituted *N*-Allyljulolidinium Halides (8)——A solution of 9-substituted julolidine **7**[4] and allyl halides in acetonitrile, acetone or methanol containing a few drops of DMF was left at rt for a prolonged period or refluxed to complete the reaction. Except in the case of **8e** the reaction mixture was evaporated and the residue was crystallized from the solvent cited in Table I. A solution of **7e** (2.02 g) and allyl bromide (7.3 g) in acetonitrile (30 ml) containing two drops of DMF was left at rt for 7 months. The brown crystals (582 mg), mp 286 °C (in a seated tube) attached to the wall of the reaction vessel were removed by filtration and the filtrate was evaporated. The residue (2.27 g) was chromatographed on silica gel (67 g) with dichloromethane containing methanol (10, 15, 20%). The first eluate (1.076 g) was rechromatographed (silica gel 26 g, dichloromethane) and **7e** (161 mg, 7.9%) was recovered. The following eluate (0.923 g) was suspended in acetone, yielding **8e** as a hygroscopic amorphous materials (622 mg, 23.6% yield). Attempts to recrystallize it from methanol, chloroform and acetone yielded only sticky materials. The product in the last eluate (0.17 g) was identical with the above unknown brown crystals (total amount: 0.75 g).

9-Hydroxyjulolidine (7b)——The phenolic portion of the products (1.1 g) obtained from the reaction of 6-methoxy-1,2,3,4-tetrahydroquinoline (10.0 g) and 1,3-bromochloropropane (58 g)[4b] was sublimed at 120 °C/4 mmHz,

giving 0.684 g of **7b**. Colorless needles, mp 123—131 °C (dec.). MS *m/z*: 189 (M^+), 188 (P^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3350, 1495, 1290, 1125. NMR δ (CD_3OD): 1.99 (4H, m, C-2-H+C-6-H), 2.71 (4H, t, J=7 Hz, C-1-H+C-7-H), 2.96 (4H, t, J=6 Hz, C-3-H+C-5-H), 6.36 (2H, s, Ar–H). Acetate: mp 92—94 °C. IR ν_{max}^{KBr} cm^{-1}: 1750, 1215. NMR δ: 1.93 (4H, m, C-2-H+C-6-H), 2.20 (3H, s, Ac), 2.73 (4H, distorted t, J=6 Hz, C-1-H+C-7-H), 3.07 (4H, distorted t, J=5.5 Hz, C-3-H+C-5-H), 6.50 (2H, s, Ar–H).

9-Ethoxyjulolidine (7c)——A solution of potassium hydroxide (4.7 g, 72 mmol) in water (5 ml) was poured into a solution of the crude **7b** (6.0 g, 31.7 mmol) and iodoethane (10.6 g, 68 mmol) in methanol (100 ml), and the mixture was stirred at r.t. for 16.5 h, then evaporated. The residue was diluted with water and extracted twice with ether. Organic extracts were washed with 1 N sodium hydroxide once then with saturated brine twice to give the crude product (3.472 g) which was subjected to Kugelrohr distillation at 165 °C/26 mmHg, affording **7c** (2.87 g, 41.6% yield) as an oil. MS *m/z*: 217 (M^+), 188 (P^+), 164. IR ν_{max}^{film} cm^{-1}: 1495, 1280, 1205, 1158, 1085, 1050, 700. NMR δ: 1.33 (3H, t, J=7 Hz, O–CH_2–CH_3), 1.97 (4H, m, C-2-H+C-6-H), 2.77 (4H, t, J=6.5 Hz, C-1-H+C-8-H), 3.05 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 3.94 (2H, q, J=7 Hz, O–CH_2–Me), 6.40 (2H, s, Ar–H). Picrate, mp 155—156.5 °C (dec.) (EtOH). *Anal.* Calcd for $C_{20}H_{22}N_4O_8$: C, 53.81; H, 4.97; N, 12.55%. Found: C, 54.04; H, 4.97, N, 12.57%.

9-Bromojulolidine (7e)——A solution of NBS (5.61 g, 0.315 mol) in dry DMF (40 ml) was poured into a solution of julolidine **1** (5.19 g, 0.03 mol) in dry DMF (60 ml) in two portions at an interval of 1 h under a nitrogen atomosphere.[8] After confirming the disappearance of julolidine by TLC after 4.5 h of reaction time, the reaction mixture was poured into water (400 ml) and basified with sodium carbonate (7 g). Extractions with ether (3 × 100 ml) and usual work-up of the extracts gave 7.1 g (94% yield) of **7e** as a colorless liquid. IR ν_{max}^{film} cm^{-1}: 1580, 1495, 1308, 1200, 883, 858, 818. NMR δ: 1.90 (4H, quintet, J=5.5 Hz, C-2-H+C-6-H), 2.70 (4H, t, J=6 Hz, C-1-H+C-7-H), 3.10 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 6.86 (2H, s, Ar–H). Hydrobromide (8.46 g, 90.5% yield): mp 223—225 °C (in a sealed tube). IR ν_{max}^{KBr} cm^{-1}: 2430, 1595, 1572, 1155, 1010, 920, 818. Hydrochloride: colorless plates, mp 216 °C (dec.) (MeOH+EtOH). IR ν_{max}^{KBr} cm^{-1}: 2280, 1598, 1572, 1158, 1012, 922, 822. NMR δ (d_6-DMSO): 1.93 (4H, quintet, J=5.5 Hz, C-2-H+C-6-H), 2.72 (4H, t, J=6 Hz, C-1-H+C-7-H), 3.20 (4H, t, J=5.5 Hz, C–3–H+C–5–H), 6.97 (2H, s, Ar–H). *Anal.* Calcd for $C_{12}H_{15}BrClN$: C, 49.94; H, 5.24; N, 4.85%. Found: C, 49.69; H, 5.13; N, 4.70%.

Rearrangement of 8a——a) The crude product (411 mg) obtained from **8a** (648 mg, 2 mmol) under condition A was separated by flash column chromatography (silica gel 45 g, petroleum ether : ethyl acetate=97 : 3). The first eluate (15 ml) contained a mixture of products. The detection of **3a** in this mixture and its identification were carried out by detailed GLC, TLC and NMR comparisons with an authentic specimen. The following eluates provided **10a** (13 mg, 2.3% yield), **9a** (271 mg, 55.7% yield) and **7a** (2 mg, 0.5% yield). 8-Allyl-9-methoxyjulolidine **9a**: Liquid. IR ν_{max}^{film} cm^{-1}: 3080, 2840, 1630. NMR δ: 1.97 (4H, m, C-2-H+C-6-H), 2.6—3.2 (8H, m, C-1-H+C-3-H+C-5-H+C-7-H), 3.33 (2H, td, J=1.5, 6 Hz, CH_2–CH=CH_2), 3.73 (3H, s, OCH_3), 4.87 and 5.10 (2H, each m, CH_2–CH=CH_2), 5.93 (1H, m, CH_2–CH=CH_2), 6.50 (1H, s, Ar–H). Hydrochloride: mp 147—150 °C (acetone–ethyl acetate). IR ν_{max}^{KBr} cm^{-1}: 3070, 2850, 2200, 1637, 1605, 1590. *Anal.* Calcd for $C_{16}H_{22}ClNO$: C, 68.68; H, 7.93; Cl, 12.67; N, 5.01%. Found: C, 68.26; H, 7.86; Cl, 12.74; N, 4.79%. 8,9-Diallyl-9-methoxyjulolidine **10a**: Liquid. MS *m/z*: 283 (M^+), 268 (P^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635, 912. NMR δ: 1.96 (4H, quintet, J=6 Hz, C-2-H+C-6-H), 2.73 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.07 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 3.43 (4H, td, J=1.5, 5.5 Hz, CH_2–CH=CH_2 × 2. Singlet when irradiated at δ 6.00), 3.57 (3H, s, OCH_3), 4.83 and 5.10 (4H, each m, CH_2–CH=CH_2 × 2), 6.00 (2H, tdd, J=5.5, 9, 18 Hz, CH_2–CH=CH_2 × 2). b) The crude product (404 mg) derived from **8a** (651 mg, 2 mmol) under condition B was flash-chromatographed on silica gel (36 g) with petroleum ether–ethyl acetate (95 : 5). The products **3a** (52 mg, 12% yield), **9a** (43 mg, 8.8% yield) and **7a** (14 mg, 3.3% yield) were isolated and identified. c) In the presence of radical scavenger: the product (204 mg, 84% yield) derived from the reaction of **8a** (325 mg, 1 mmol) under condition B in the presence of 4,4′-thiobis (6-*tert*-butyl-*m*-cresol) (12 mg) in an atmosphere of argon was shown by TLC, GLC and GC-MS to contain **7a** (17.4%), **9a** (37.0%) and **3a** (42.6%).

Rearrangement of 8f——The iodide **8f** (746 mg, 2 mmol) allowed to react in the presence of sodium hydrogen carbonate (187 mg, 2.2 mmol). The crude product (413 mg) was subjected to flash column chromatography (silica gel 34 g, petroleum ether : ethyl acetate=97 : 3, 95 : 5). The products **3a** (30 mg), **9a** (42 mg) and **7a** (35 mg) isolated were identified by comparison with authentic specimens by GLC, TLC and NMR.

8-Propyl-9-methoxyjulolidine——Prepared by the catalytic hydrogenation of **9a**. mp 52.5—54.0 °C. MS Calcd for $C_{16}H_{23}NO$: 245.1780. Measured: 245.1784. IR ν_{max}^{KBr} cm^{-1}: 2870, 2850, 1488. NMR δ: 1.97 (3H, d, J=6.5 Hz, CH_2–CH_3), 1.47 (2H, m, CH_2–CH_2–Me), 1.97 (4H, m, C-2-H+C-6-H), 2.3—3.2 (10H, m, C-1-H+C-3-H+C-5-H+C-7-H+Ar–CH_2–Et), 3.72 (3H, s, OCH_3), 6.46 (1H, s, Ar–H).

Rearrangement of 8b——The crude product (444 mg) obtained by the reaction of **8b** (623 mg, 2 mmol) under condition A was crystallized from ether–petroleum ether to give 201 mg (53% yield) of 8-allyl-9-hydroxyjulolidine **9b**: mp 67—75 °C. MS Calcd for $C_{15}H_{19}NO$: 229.1467. Measured: 229.1460. IR ν_{max}^{KBr} cm^{-1}: 3400—2600, 3080, 1638, 1290, 1198, 910, 710. NMR: broad indistinguishable signals. Hydrochloride: mp 204—215 °C (dec.) (MeOH–acetone). The acetate (196 mg) was prepared by the treatment of **9b** (246 mg) with a mixture of acetic anhydride (3 ml) and pyridine (3 ml) at 90 °C for 1 h, followed by purification of the crude product (254 mg) on silica gel (8 g) with dichloromethane in 67% yield. Liquid. MS *m/z*: 271 (M^+). IR ν_{max}^{film} cm^{-1}: 3080, 2782, 1743, 1637, 1200, 912. NMR δ:

1.95 (4H, m, C-2-H+C-6-H), 2.24 (3H, s, Ac), 2.71 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.11 (6H, m, C-3-H+C-5-H+$C\underline{H}_2$–CH=CH_2), 4.84 and 5.08 (2H, each m, CH_2–CH=$C\underline{H}_2$), 5.77 (1H, m, CH_2–$C\underline{H}$=CH_2. Double d, J= 10, 17 Hz on irradiation at δ 3.20), 6.56 (1H, s, Ar–H).

Rearrangement of 8c——a) The crude product (436 mg) obtained by the reaction of **8c** (676 mg, 2 mmol) under condition A was separated by flash column chromatography on silica gel (45 g) with petroleum ether–ethyl acetate (95 : 5) to provide **10c** (24 mg, 4.0% yield), **9c** (325 mg, 63.2% yield) and a mixture of **9c** and **7c** (62 mg, 43 : 57). 8,10-Diallyl-9-ethoxyjulolidine **10c**: Oil. MS m/z: 297 (M^+), 258 (P^+). NMR δ: 1.36 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.96 (4H, m, C-2-H+C-6-H), 2.70 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.06 (4H, t, J=5.5 Hz, C-3-H+C-5-H), 3.37 (4H, td, J=1.5, 5.5 Hz, Ar–$C\underline{H}_2$–CH=CH_2 × 2), 3.76 (2H, q, J=7 Hz, $OC\underline{H}_2$–Me), 4.87 and 5.10 (4H, each m, Ar–CH_2–CH=$C\underline{H}_2$ × 2), 5.97 (2H, m, Ar–CH_2–$C\underline{H}$=CH_2 × 2). 8-Allyl-9-ethoxyjulolidine **9c**: Liquid. MS m/z: 257 (M^+), 228 (P^+). IR ν_{max}^{film} cm^{-1}: 1638, 1430, 1275, 1207, 1115, 1030, 900. NMR δ: 1.33 (3H, t, J=7Hz, OCH_2–$C\underline{H}_3$), 1.97 (4H, m, C-2-H+C-6-H), 2.73 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.00 (4H, m, C-3-H+C-5-H), 3.33 (2H, td, J=1.5 Hz, Ar–$C\underline{H}_2$–CH=CH_2), 3.93 (2H, q, $OC\underline{H}_2$–Me), 4.83 and 5.07 (2H, each m, Ar–CH_2–CH=$C\underline{H}_2$), 5.90 (1H, tdd, J=6, 9, 17 Hz, Ar–CH_2–$C\underline{H}$=CH_2), 6.43 (1H, s, Ar–H). Hydrochloride: fine needles, mp 135—143 °C (dec.). *Anal.* Calcd for $C_{17}H_{24}ClNO$: Cl, 12.06%. Found: 11.41%. b) The crude product (357 mg) derived from the reaction of **8c** (677 mg) under condition B was similarly chromatographed to give **3a** (91 mg, 21.3% yield), **9c** (63 mg, 12.2% yield) and a mixture of **9c** and **7c** (17 mg, 76 : 24).

Rearrangement of 8d——The reaction of **8d** (616 mg, 2 mmol) under condition B gave a brown liquid product (288 mg), which darkened gradually on standing. Preparative GLC of the crude product on 20% SE-30 (stainless steel column 5 mm × 1 m) at 230 °C under nitrogen (50 ml/min) afforded **7d** (52 mg) and 8-allyl-9-methyljulolidine **9d** as a liquid. **9d**: MS Calcd for $C_{16}H_{21}N$: 227.1674. Found: 227.1663. IR ν_{max}^{film} cm^{-1}: 3090, 1638, 1495, 1308, 910. NMR δ: 1.97 (4H, m, C-2-H+C-6-H), 2.17 (3H, s, Ar–CH_3), 2.77 (4H, t, J=6 Hz, C-1-H+C-7-H), 3.07 (4H, m, C-3-H+C-5-H), 3.30 (2H, td, J=2, 6 Hz, Ar–$C\underline{H}_2$–CH=CH_2), 4.70 and 5.10 (2H, each m, Ar–CH_2–CH=$C\underline{H}_2$), 5.93 (1H, m, Ar–CH_2–$C\underline{H}$=CH_2), 6.70 (1H, s, Ar–H).

2-Methyl-2,3-dihydrofuro[2,3-*i*]julolidine (11)——a) A solution of crude **9a** (624 mg) in 47% hydrobromic acid (15 ml) was refluxed for 4 h. After basification with sodium carbonate the reaction mixture was extracted with ether three times. The extract (537 mg) was purified by column chromatography on silica gel (12 g) with dichloromethane containing increasing amounts of acetone (0, 1, 2%) to give **11** (302 mg, 51.4% yield) as an oil. IR ν_{max}^{film} cm^{-1}: 2840, 2810, 2770, 1600, 1205, 1010. NMR δ: 1.90 (3H, d, J=6 Hz, $CHC\underline{H}_3$), 2.00 (4H, m, C-2-H+C-6-H), 2.4—3.3 (10H, m, CH_2 × 5), 4.80 (1H, m, CH_2–$C\underline{H}$–Me. Triplet, J=8 Hz on irradiation at δ 1.40), 6.26 (1H, s, Ar–H). Hydrochloride: colorless needles, mp 188—200 °C (dec.) (methanol–acetone). IR ν_{max}^{KBr} cm^{-1}: 2150, 1602, 1005, 845. *Anal.* Calcd for $C_{15}H_{20}ClNO$: C, 67.79; H, 7.58; Cl, 13.34; N, 5.27%. Found: C, 67.60; H, 7.66; Cl, 13.50; N, 5.14%. b) A solution of **9b** (51 mg) in 47% hydrobromic acid (2 ml) was refluxed for 3 h. The crude product (38 mg) was purified similarly to give 27 mg (53% yield) of **11**. c) The similar reaction of **9d** (92 mg) gave **11** in 62.7% yield.

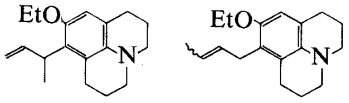
Rearrangement of 8e——The crude product (123 mg) obtained from **8e** (373 mg, 1 mmol) under reaction condition B and that (73 mg) obtained from **8e** (191 mg, 0.5 mmol) under condition A were combined and chromatographed on silica gel (9 g) with bezene. The first eluate (16 mg) contained **7e** and the following eluate (119 mg) contained **3a**, which was identified by IR, NMR, and TLC as well as by mmp of the hydrobromide, mp 186—187 °C.

9-Methoxy-*N*-crotyljulolidinium Bromide (12)——A solution of 9-methoxyjulolidine (1.60 g, 7.9 mmol) and crotyl bromide (10.0 g, 74 mmol; containing 15% 3-bromo-1-butene) in acetone (40 ml) was left at rt overnight then refluxed for 1 h. The reaction mixture was evaporated and the residue was crystallized by the addition of ethanol to give crystalline **12** (2.30 g, 86% yield).

Rearrangement of 12——a) The bromide **12** (677 mg, 2 mmol) was reacted under reaction condition A for 4 h. The crude product (340 mg) was chromatographed on silica gel (17.5 g) with dichloromethane containing acetone (0, 1%) to give a mixture (177 mg, **13**: *E*-**14**: *Z*-**14** = 20 : 62 : 18) and **7a** (68 mg, 16.7% yield). b) The crude product (176 mg) obtained by the reaction of **12** (269 mg, 0.8 mmol) under reaction condition B in an atmosphere of nitrogen was separated by column chromatography (silica gel 9.0 g, dichloromethane). The isomeric mixture **3b** (E : Z = 4 : 5 6 mg, 3.3% yield), a mixture of **13** and **14** (72 mg, 35% yield) and **7a** (18 mg, 11.1% yield) were isolated and identified by NMR comparisons with authentic specimen. A mixture of **13** and **14** (188 mg) was preparatively separated by GLC on 20% SE-30 (stainless steel column, 6 mm × 2 m) at 210 °C under helium (33 ml/min) to give **13** (4 mg, t_R = 8.2 min), *E*-**14** (20 mg, t_R = 10.0 min) and *Z*-**14** (3 mg, t_R = 11.5 min) with more than 99% purity. 9-Methoxy-8-(1-methyl-2-propenyl)julolidine **13**. MS Calcd for $C_{17}H_{23}NO$: 257.1779. Found: 257.1762. IR ν_{max}^{film} cm^{-1}: 3070, 2845, 1605, 1640, 907, 835. NMR δ: 1.37 (3H, d, J=7 Hz, CH–$C\underline{H}_3$. Singlet on irradiation at δ 4.00), 1.97 (4H, m, C-2-H+C-6-H), 2.80 (4H, t, J=6.5 Hz, C-1-H+C-7-H), 3.03 (4H, m, C-3-H+C-5-H), 3.76 (3H, s, OCH_3), 4.00 (1H, m, CH_2=CH–$C\underline{H}$–Me. Doublet, J=7 Hz with small allylic couplings when irradiated at δ 1.37), 4.8—5.2 (2H, m, $C\underline{H}_2$=CH–CH–Me), 6.30 (1H, m, CH_2=$C\underline{H}$–CH–Me), 6.50 (1H, s, Ar–H). 8-(*E*-2-Butenyl)-9-methoxyjulolidine *E*-**14**. MS Calcd for $C_{17}H_{23}NO$: 257.1779. Found: 257.1763. IR ν_{max}^{film} cm^{-1}: 1665, 880, 830. NMR δ: 1.63 (3H, m, CH–$C\underline{H}_3$. Singlet on irradiation at δ 5.37), 1.97 (4H, m, C-2-H+C-6-H), 2.77 (4H, m, C-1-H+C-7-H), 2.93 (2H, m, Ar–$C\underline{H}_2$–CH=. Singlet on irradiation at δ 5.37), 3.73 (3H, s, OCH_3), 5.37 (2H, m, Ar–CH_2–$C\underline{H}$=$C\underline{H}$–Me), 6.40 (1H,

s, Ar–H). 8-(*Z*-2-Butenyl)-9-methoxyjulolidine *Z*-**14**. MS Calcd for $C_{17}H_{23}NO$: 257.1779. Found: 257.1769. IR ν_{max}^{film} cm^{-1}: 1661, 975, 882, 833, 707. NMR δ: 1.77 (3H, s, $J=5$ Hz, CH_3–CH=. Singlet on irradiation at δ 5.37), 2.00 (4H, m, C-2-H+C-6-H), 2.76 (4H, m, C-1-H+C-7-H), 3.36 (2H, d, $J=5$ Hz, with small allylic couplings. Ar–CH_2–CH=), 3.76 (3H, s, OCH_3), 5.37 (2H, m, Ar–CH_2–CH=CH–Me), 6.43 (1H, s, Ar–H). The crude product (**7a**:**13**:*E*-**14**:*Z*-**14**=35:12:39:12, 93 mg) was hydrogenated over 5% Pd–C in ethanol and the product (**7a**:**15**:**16**=35:13:51) was separated by chromatography (silica gel 3.2 g) with dichloromethane to give a mixture of **15** and **16** (29 mg). IR ν_{max}^{film} cm^{-1}: 2870, 2780, 1486, 1462, 1210, 1115, 1050. GC-MS **15**: $t_R=1.75$ min, *m/z*: 259 (M^+), 244, 215, 108; **16**: $t_R=2.87$ min, *m/z*: 259 (M^+), 244, 202, 172, 130. NMR δ: Signals for **15**: 0.93 (3H, distorted t, $J=$ 7 Hz, CH_2–CH_3), 1.40 (4H, m, Ar–CH_2–CH_2–CH_2–Me), 2.00 (4H, m, C-2-H+C-6-H), 2.53 (2H, m, Ar–CH_2–Pr), 3.00 (8H, m, C-1-H+C-3-H+C-5-H+C-7-H), 3.70 (3H, s, OCH_3), 6.40 (1H, s, Ar–H); Signals for **16**: 1.26 (d, $J=$ 7 Hz, CH–CH_3. Singlet on irradiation at δ 2.86), 3.68 (s, OCH_3).

Crossover Reactions——a) A mixture of **8f** (380 mg, 1.0 mmol) and julolidine **1** (176 mg, 1 mmol) was reacted under condition A for 4 h. The crude product (380 mg) was analyzed by GLC (10% SE-30 and 15% QF-1; 3 mm × 2 m; 210 °C; nitrogen 30 ml/min) in comparison with authentic specimens and was found to be a mixture of **1** (48%), **7a** (8%), **3a** (2%), **9a** (40%) and an unidentified product (3%). b) A mixture of **8c** (60 mg) and **12** (60 mg) (total amount 120 mg, 0.35 mmol) in glycerol–water (2/1, 1 ml) was reacted under condition A. For reaction condition B, sodium hydrogen carbonate (31 mg, 0.37 mmol) was added to the reaction mixture, and the reaction vessel was evacuated to replace air with argon prior to reaction. The crude products were analyzed by GLC (10% SE-30 and 15% QF-1) and the products were identified by GC-MS comparisons with authentic specimens, if available. Except for **9a**, no specimen of crossover reaction products was available but their presence was deduced from the retention



17 **18**

React. cond.	Crude yield (%)	Intramolecular reaction products									Crossover products		
		7a	**7c**	**3a**	*E*-**3b**	*Z*-**3b**	**9c**	**13**	*E*-**14**	*Z*-**14**	**9a**	**17**	**18**
A	88	20.7	7.4	—	—	—	45.0	2.3	18.1	4.3	2.5	—	—
B	82	16.6	5.6	15.7	2.4	3.0	28.8	6.4	17.2	4.2	—	—	—

times (t_R) estimated from the t_R differences between the known compounds under consideration and the structural differences.

References and Notes

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