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Amino-Claisen Rearrangement. I

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Investigation of pyrolytic reactions of N-allylanilinium salts led to the finding of a new type of amino-Claisen rearrangement, aromatic ammonium N-Claisen rearrangement. This reaction enables the introduction of functional group into the *ortho* position of aniline derivatives. Products are potential precursors for indoline and indole preparations.

Keywords——N-allyl-N,N-dimethylanilinium salts; pyrolysis; amino-Claisen rearrangement; *ortho*-allyl-N,N-dimethylaniline derivatives; indolines

Claisen rearrangement has been a subject of many dedicated chemists for decades and led to the explorations of many valuable synthetic methods.[2] It can be classified, according to the species of hetero atoms involved, into oxo-, amino- and thio- Claisen rearrangement (I), among which amino(N)-Claisen rearrangement has attracted the least attentions. Although much milder reaction conditions are searched for elegant N-Claisen rearrangement,[3a] in general it requires vigorous heating, thus leads to poor results.[3b] This unfavorable reaction condition is sometimes avoided by introducing acid catalyst.[4] Exploring the role of this acid catalysis Schmid has reached to the finding of "Charge Induced Claisen Rearrangement".[5] This type of rearrangement can be regarded as onium Claisen rearrangement (II). Works intended in this area are quite scarce. There is a single paper concerned with sulfonium thio-Claisen rearrangement.[6] (II: Y=S) For ammonium N-Claisen rearrangement (II: Y=NR) a few proposals as reaction intermediates have been reported in aliphatic series.[2a] Schmid has offered so far a single case for aromatic ammonium N-Claisen rearrangement.[5] More recently Hansen has reported detailed investigations of N-Claisen rearrangement accelerated by the presence of sulfuric acid, *e.g. in situ* generation of ammonium salt.[7] In 1971 we have had also found this new type of N-Claisen rearrangement during the detailed investigation

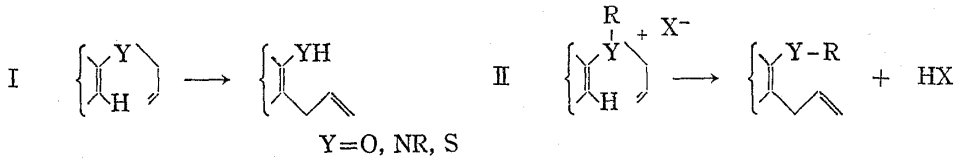


Chart 1

1) Location: *Edmonton, Alberta, Canada*; Present address: *Niigata College of Pharmacy, 5829 Kamishin'ei-Cho, Niigata 950-21, Japan.*
2) *a*) S.J. Rhoads and N.R. Raulins, "Organic Reactions," vol. 22, ed. by W.G. Dauben, John Wiley and Sons, Ind., New York, 1975, p. 1; *b*) A. Jefferson, *Quart. Rev.* (London), **22**, 391 (1968); *c*) D.C. Tarbell, "Organic Reactions," vol. 2, ed. by R. Adams, 1944, p. 1; d) F.E. Ziegler, *Accounts Chem. Res.*, **10**, 227 (1977).
3) *a*) R.M. Coats and I.Md. Said, *J. Am. Chem. Soc.*, **99**, 2355 (1977); *b*) S. Marcinkiewicz, J. Green and P. Mamalis, *Tetrahedron*, **14**, 208 (1961): *Chem. Ind.* (London), **1961**, 438.
4) *a*) S. Inoue, N. Takamatsu and Y. Kishi, *Yakugaku Zasshi*, **97**, 553 (1977); *b*) S. Inoue, N.Takamatsu and Y. Kishi, *ibid.*, **97**, 558 (1977); *c*) S. Inoue, N. Takamatsu and Y. Kishi, *ibid.*, **97**, 564 (1977); *d*) C.D. Hurd and W.W. Jenkins, *J. Org. Chem.*, **27**, 1109 (1962).
5) M. Schmid, H-J. Hansen and H. Schmid, *Helv. Chim. Acta.*, **56**, 105 (1973).
6) B.W. Bycraft and W. Landon, *Chem. Commun.*, **1970**, 967.
7) S. Jolidon and H-J. Hansen, *Helv. Chim. Acta.*, **60**, 978 (1977).

of the pyrolytic reactions of N-allyl-N,N-dimethylanilinium derivatives. In this report we would like to present our findings and the scope of ammonium N-Claisen rearrangement of aromatic compounds.

Pyrolysis of Allylanilinium Salts

When 4-hydroxy-N-allyl-N,N-dimethylanilinium bromide **1** was heated to 200° under nitrogen atmosphere an air-sensitive compound **3** was produced besides deallylated product **2**. Its hydrochloride **3**: HCl mp 213—217° has a *sec*-methyl (NMR δ: 1.64, doublet, J=6.5 Hz) and an N-methyl groups (δ: 3.20, singlet) along with three aromatic protons (δ: 6.90, 2H, multiplet; 7.40, 1H, doublet, J=9 Hz). Its acetate **4**, mp 63—64° showed composition $C_{12}H_{15}NO_2$ and molecular weight 205.1099 (Calcd. 205.1102) and three aromatic protons in 1,2,4-relation (δ: 6.37, 1H, doublet, J=9 Hz; 6.78, 1H, multiplet; 6.79, 1H, quartet, J=9, 3 Hz). These observations indicated the indoline structure and in fact acetate **4** was dehydrogenated into 1,2-dimethyl-5-acetoxyindole **5** which was identified with authentic specimen synthesized by Nenitzescu method.[8] Hydrobromide of 1,2-dimethyl-5-hydroxyindoline **3**: HBr was also obtained from pyrolysis residue. Formation of 1,2-dimethylindoline skeleton suggests the possible ammonium N-Claisen rearrangement when one considers the occasional contamination of dihydrobenzofurans in Claisen rearrangement. In order to remove the intermediate quickly 4-hydroxy-N-allyl-N,N-dimethylanilinium hydroxide **6** was steam-distilled to get deallylated product **2** and new products **7** and **8** in 10, 34 and 26% yield respectively. New products **7** and **8** were characterized in acetate **9** and **10**. These two products have the same number of substituents and were considered to be the positional isomer of allyl group of nuclear-allylated 4-hydroxy-N,N-dimethylaniline. One of these products **8** was then identified with the specimen derived from the Claisen rearrangement of 4-allyloxy-N,N-dimethylaniline **11**.[9] The other isomer **7** was thus 2-allyl-4-hydroxy-N,N-dimethylaniline and alternatively prepared by ammonium N-Claisen rearrangement of **1**, *vide infra*.

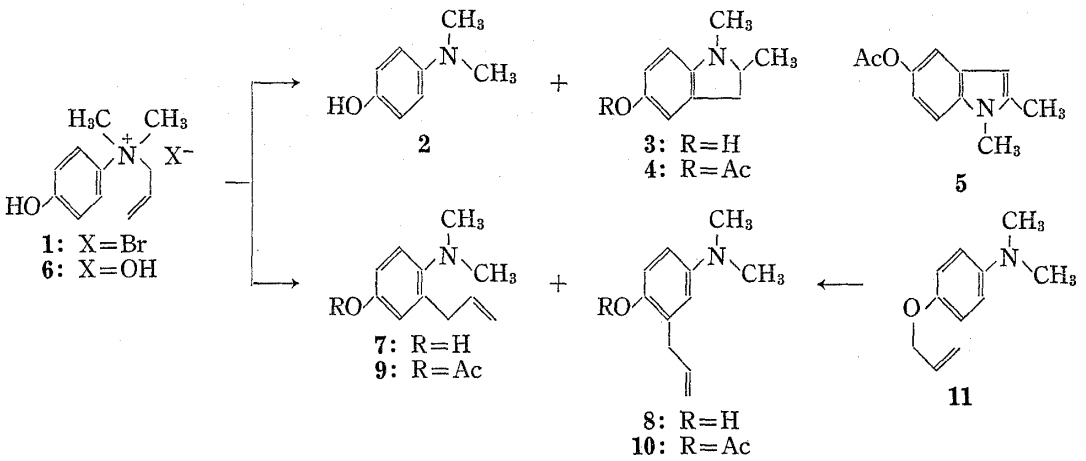


Chart 2

Similarly the pyrolysis of N-allyl-N,N-dimethylanilinium bromide **12** at 140° under nitrogen gave a mixture of N,N-dimethyl aniline **13**, N-allyl-N-methylaniline **14** and 1,2-dimethylindoline **15** in 67, 10 and 6% yield. Reaction in N,N-dimethylaniline at 145° gave N-allyl-N-methylaniline **14** and 1,2-dimethylindoline **15** in 60 and 23% yield. These observations prompted us to investigate the reaction condition suitable for possible ammonium N-Claisen rearrangement.

8) E.A. Steck, R.P. Brundage and L.T. Fletcher, *J. Org. Chem.*, **24**, 1750 (1959).
9) H.L. Goering and R.R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

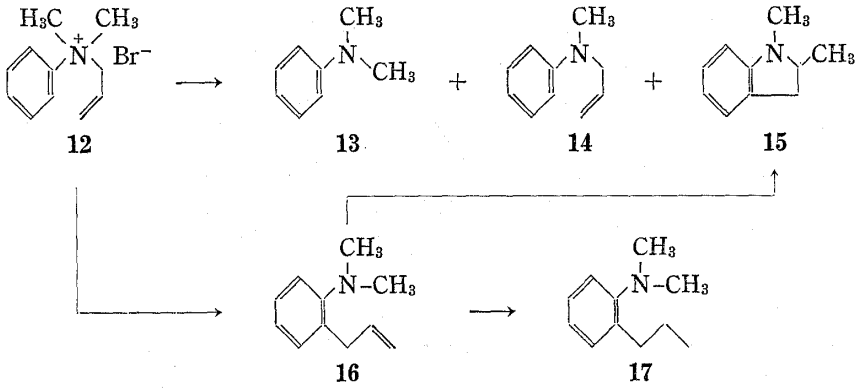
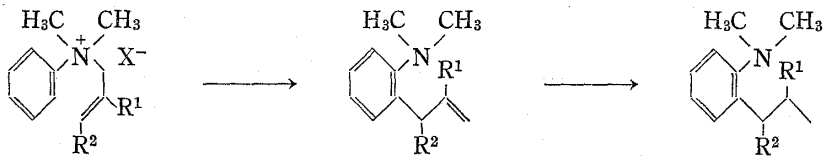


Chart 3

N-Claisen Rearrangement of Allylanilinium Salts

After checking the reaction conditions such as solvent, reaction temperature, reaction time and the need of additives by using N-allyl-N,N-dimethylanilinium bromide **12** we found that ammonium N-Claisen rearrangement in fact takes place and its yield is quite depending on the polarity of solvent. Thus the rearrangement of **12** in dimethylformamide at 135° for 2 hr gave **16** in 2% but the employment of glycerin improved the yield to 34%. Further improvement was achieved by polarity increase by adding water (glycerin/water=2/1) to 53%. Presence of sodium bicarbonate to remove acid generated is effective to 81% but attention is due to phenolic salts, *vide infra*. In practice ammonium salt was heated in glycerin–water (2/1) at 140° (bath temperature) for 2—4 hr under nitrogen either in the absence (condition A) or in the presence of an equimolar amount of sodium bicarbonate (condition B). Generally condition B gives better result when applicable. The structure of **16** was suggested by the number of aromatic protons (NMR δ: 7.10, 4H, singlet) and the presence of allyl group (IR ν_{max}^{film} cm^{-1}: 3070, 1634. NMR δ: 3.49, 2H, doublet, J=6.5 Hz; 4.96 and 5.18, 2H, each broad multiplet; 6.03, 1H, triplet of quartet, J=6, 9, 17.5 Hz). Product **16** was hydrogenated to *o*-propyl-N,N-dimethylaniline **17**[10] identical with authentic specimen prepared by the hydrogenation of Hoffman degradation product of 1,1,2 trimethylindolinium bromide with potassium *t*-butoxide. Also 2-allyl-N,N-dimethylaniline was transferred into 1,2-dimethylindoline **15** in 85% yield by hydrochloric acid. Substituted allyl-N,N-dimethylanilinium compounds **18** and **20** also rearranged in a similar manner into *ortho*-allylated product **19** and **21** (condition B). The formation of **19** strongly suggests the intramolecular [3, 3] sigmatropic rearrangement for this N-Claisen rearrangement. Products were also confirmed by physical methods as well as hydrogenation into corresponding saturated derivatives.



12: R^1=R^2=H, X=Br
18: R^1=H, R^2=Me, X=Br
20: R^1=Me, R^2=H, X=Cl

16: (53%)
19: (55%)
21: (88%)

Chart 4

4-Hydroxy-N-allyl-N,N-dimethylanilinium bromide **1** in condition A gave, as indicated in the pyrolytic reaction, air-sensitive phenol **7** in 54% yield which was transfered into stable acetate **9**. Rearrangement in condition B yielded isomeric phenol **8** (46%) along with *p*-di-

10) D.A. Archer, H. Booth, P.C. Crisp and J. Parrick, *J. Chem. Soc.*, **1963**, 330.

methylaminophenol **2** (4%) and a new phenolic product **22**. A new product **22** (MS M^+ *m/e*: 217) has two allyl groups (NMR δ: 3.38, 4H, doublet, J=6 Hz; 5.00 and 5.24, 4H, each broad singlet; 6.06, 2H, triplet of quartet, J=6, 9, 17 Hz), two N-methyl groups (δ: 2.85, 6H, singlet) and a hydroxyl group ($\nu_{max}^{CHCl_3}$ cm^{-1}: 3530, no free OH absorption. δ: 5.27, 1H, singlet, D_2O exchanged) as well as singlet aromatic signal corresponding to two protons (δ: 6.51). These observations coincide with symmetrical 2,6-diallyl-4-dimethylaminophenol **22**. Formation of **8** and **22** were also observed in the pyrolysis of 4-hydroxy-N-allyl-N,N-dimethylanilinium hydroxide **6** at 210° and of sodium salt of 4-hydroxy-N-allyl-N,N-dimethylanilinium bromide **1** at 190°. In condition B phenolic anilinium salt reacts at first with N-allylquaternary salt to form allylphenol ether *via* intermolecular O-allylation.[11] Subsequent Claisen rearrangement leads to *o*-allylated phenol **8**. Thus the reaction condition for phenolic anilinium salt is critical for product pattern, *e.g.* condition A leads to N-Claisen and condition B to O-Claisen rearrangement.

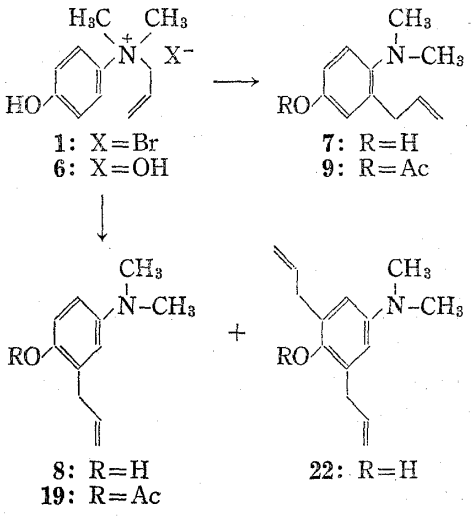


Chart 5

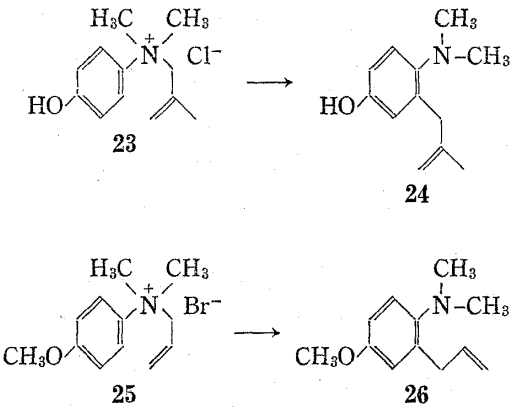


Chart 6

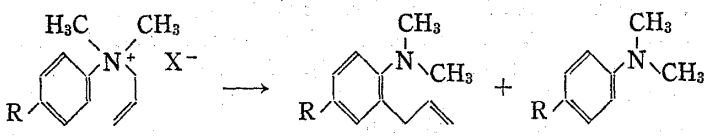
4-Hydroxy-N-isobutenyl-N,N-dimethylanilinium chloride **23** in condition A afforded 2-isobutenyl-4-hydroxy-N,N-dimethylaniline **24**. For 4-methoxy-N-allyl-N,N-dimethylanilinium bromide **25** N-Claisen rearrangement proceeds in both conditions: A in 50% and B in 57% yield to give 2-allyl-4-methoxy-N,N-dimethylaniline **26** which was identical with methyl ether derived from the N-Claisen rearrangement of **1** and subsequent methylation with diazomethane.

At this stage attention was turned to the counter ion effects (Table I). In either reaction condition non-phenolic anilinium salts show the similar trend to counter ions – increase in nucleophilicity of halides drops the yield of rearrangement, slightly from chlorine to bromide but remarkably from bromine to iodine. Introduction of poor nucleophile such as BF_4^- does not increase the yield of rearrangement product but quality. Tetraphenylborate BPh_4^-, non-nucleophilic anion has problem in solubility but its reaction in dimethylformamide led to competitive result.

New type of ammonium N-Claisen rearrangement presented here may be [3, 3] sigmatropic rearrangement as in ordinary Claisen rearrangement. This mechanism is strongly supported by the rearrangement feature of N-crotyl salt **18**. In conclusion we have presented a new type of N-Claisen rearrangement. It enables for aniline derivative to introduce *ortho*-

11) S. Tarbell and J.R. Vaughan, Jr., *J. Am. Chem. Soc.*, **65**, 231 (1943).

Table I. Counter Ion Effects



R=	X=		Reaction conditions[a]		Yield[b] (%)		
OH	Cl		A	**7** 47	**2** —		
OH	Br	**1**	A	**7** 47	**2** 1		
OH	I		A	**7** 19	**2** 8		
OMe	Cl		B	**26** 61	2		
OMe	Br	**25**	B	**26** 60	7		
OMe	I		B	**26** 43	9		
H	Br	**12**	A	**16** 53	**13** 9		
			B	**16** 81	**13** 9		
H	BF_4		A	**16** 75	**13** 2		
H	BPh_4		A[c]	**16** 20	**13** 71		
			[d]	**16** 78	**13** 12		

a) Quaternary salt (2.0 mmol) in a mixture of glycerin-water (2/1, 6 ml) was heated to 135° (bath temperature) for 2—4 hr under nitrogen either in the absence (A) or in the presence (B) of an equimolar sodium bicarbonate.
b) Yields were determined by GLC analysis (20% and 10% SE-30, 10 ft by 1/8 inch at 170°).
c) Reaction was carried out in a sealed tube at 150°.
d) Salt and DMF in a sealed tube was heated to 145° for 5.5 hr.

allyl and other functional groups. Products are potential precursors for indoline and indole preparations. The effects of *ortho*- substituents on ammonium N-Claisen rearrangement of aromatic amines are under investigation and will be published in future issue.

Experimental

Anilinium salts were prepared by treating aniline derivatives with excess allyl halides in methylacohol and acetone. All melting points were taken on hot stage apparatus and are uncorrected. Physical measurements were carried out by using Perkin-Elmer model 421 dual grating spectrometer and Perkin-Elmer model 337 grating spectrometer for infrared (IR) spectra, Cary model 14M spectrophotometer for Ultraviolet (UV) spectra, Varian A-60 and HA-100 spectrometer for nuclear magnetic resonance (NMR) spectra, A.E.I. model-9 high resolution mass spectrometer and A.E.I. Mass (MS) spectra and Varian Aerograph gass chromatograph model A-90-P3 for gas–liquid chromatography (GLC). NMR were measured in deuterochloroform with tetramethylsilane as internal standard unless otherwise noticed. UV were taken in MeOH. GLC were carried out by 20% and 10% SE-30 and 20% QF-1 as liquid phase supported on chromosorb and uniport B column (10 ft by 1/8 inch and 2m by 3 mm) with helium and nitrogen as carrier gas. Skellysolve B refers to Skelly Oil Company petroleun bp 62—70°. Analysis were done at Microanalytical Laboratory of this department. Abbreviation used: s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, sex=sextet and m=multiplet.

4-Hydroxy-N-allyl-N,N-dimethylanilinium Bromide 1——Freshly distilled *p*-dimethylaminophenol (19.27 g) was treated with excess allylbromide at room temperature to give quaternary bromide (24.02 g). Recrystallization from MeOH yielded **1**, colorless rod, mp 157.5—161°. IR ν_{max}^{KBr} cm^{-1}: 3420, 3100, 1612. NMR (CD_3OD) δ: 3.64 (6H, s, NMe_3), 4.54 (2H, d, J=6 Hz, $-CH_2-$), 5.63 (3H, m, $CH{=}CH_2$), 7.02 and 7.71 (4H, A_2B_2, J=9.5 Hz, Ar-H). *Anal.* Calcd. for $C_{11}H_{16}BrNO$: C, 51.18; H, 6.25; N, 5.43; Br, 30.95. Found: C, 51.23; H, 6.11; N, 5.39; Br, 30.78.

Pyrolysis of 4-Hydroxy-N-allyl-N,N-dimethylanilinium Bromide 1——Bromide (5.028 g) was heated at 200° under nitrogen, then distilled at 230° in water vaccum to give distillate I (1.794 g) and II (1.444 g). Distillate I was chromatographed on silica gel (60 g) with the combination of chloroform and acetone to give homogeneous fraction (0.374 g) which was distilled at 100—133°/0.85 mmHg to give 1,2-dimethyl-5-hydroxyindoline **3**, colorless oil. IR ν_{max}^{film} cm^{-1}: 3360, 1602. Hydrochloride **3**: HCl, fine needle, recrystallized from MeOH–acetone, mp 213—217°. UV λ_{max} nm (ε): 243 (1560), 277 (1500). IR ν_{max}^{KBr} cm^{-1}: 2430, 1610. NMR (CD_3OD) δ: 1.64 (3H, d, J=6.5 Hz, *sec*-Me), 3.20 (3H, s, NMe), 6.90 (2H, m, Ar-H), 7.40 (1H, d, J=9 Hz, Ar-H). *Anal.* Calcd. for $C_{10}H_{14}ClNO$: C, 60.15; H, 7.07; N, 7.02; Cl, 17.75. Found: C, 60.10; H, 6.98; N, 7.07; Cl, 17.64. Crystal appeared in distillate II was collected and recrystallized from MeOH to give hydro-

bromide **3**: HBr (0.607 g), colorless rod, mp 231—234°/UV λ_{max} nm (ε): 242 (3200), 275 (2200). IR ν_{max}^{KBr} cm^{-1}: 3400, 2700—2400. *Anal.* Calcd. for $C_{10}H_{14}BrNO$: C, 49.20; H, 5.78; N, 5.74; Br, 32.73. Found: C, 48.97; H, 5.57; N, 5.66; Br, 33.03. Acetate **4**, colorless plate, recrystallized from ether-Skellysolve B, mp 63—64°. UV λ_{max} nm (ε): 257.5 (5600), 306 (1500). IR ν_{max}^{KBr} cm^{-1}: 1757, 1208. NMR δ: 1.28 (3H, d, J=6 Hz, *sec*-Me), 2.23 (3H, s, COMe), 2.67 (3H, s, NMe), 6.37 (1H, d, J=9 Hz, Ar-H), 6.78 (1H, m, Ar-H), 6.79 (1H, q, J=9 and 3 Hz, Ar-H). MS Calcd. for $C_{12}H_{15}NO_2$: 205.1102. Measured: 205.1109. *Anal.* Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.08; H, 7.38; 7.05. Hydrochloride of acetate **4**: HCl, colorless plate, recrystallized from MeOH–acetone, mp 127—135°. IR ν_{max}^{KBr} cm^{-1}: 3440, 2350, 1760. NMR (CD_3OD) δ: 1.67 (3H, d, J=6.5 Hz, *sec*-Me), 2.32 (3H, s, COMe), 7.27 (1H, q, J=2, 9.5 Hz, Ar-H), 7.30 (1H, d, J=2 Hz, Ar-H), 7.61 (1H, d, J=9.5 Hz, Ar-H).

Dehydrogenation of 1,2-Dimethyl-5-acetoxyindoline 4——4 (218 mg) and 5% Pd-C (73 mg) were gradually heated to 210° and kept at 200—210° for 45 min. Methanol and chloroform soluble part (197 mg) was purified on silica gel (7 g) with chloroform–acetone (95/5) to give solid (152 mg) which was recrystallized from ether-Skellysolve B and sublimed at 83—95°/1.5 mmHg to give 1,2-dimethyl-5-acetoxyindole **5**, mp 99—101.5°, identical with synthetic specimen[8] by IR, NMR and mmp comparisons.

Steam Distillation of 4-Hydroxy-N-allyl-N,N-dimethylanilinium Hydroxide 6——Bromide **1** (5.00 g) was treated with silver oxide (4.5 g) in water (50 ml) for two days. Filtrate was steam-distilled and distillate was extracted with ether and chloroform. Ethereal extract (1.977 g), consisting of **2** (3%), **7** (55%) and **8** (37%) on GLC, was subjected to chromatography on silica gel (60 g) with the aid of chloroform and acetone. First eluate (363 mg) was purified on silica gel (50 g) again to give 2-allyl-4-hydroxy-N,N-dimethylaniline **7** (170 mg) identical with the specimen prepared by N-Claisen rearrangement of **1**, *vide infra* by IR and NMR behaviors. Following eluate (402 mg) was 3-allyl-4-hydroxy-N,N-dimethylaniline **8** identified in free and acetate states by IR comparisons. The most polar fraction (73 mg) was N,N-dimethyl-4-hydroxyaniline **2** identified as acetate.

Claisen Rearrangement of 4-Allyloxy-N,N-dimethylaniline 11——Allylether **11** (620 mg. Hydrochloride mp 117.5—122.5°)[9] was heated in a glass tube at 200° for 5 hr. Phenolic portion of product (387 mg) was chromatographed on silica gel (9 g) with chloroform–acetone to give 3-allyl-4-hydroxy-N,N-dimethylaniline **8** (196 mg), bp 112—114°/2.5 mmHg. IR $\nu_{max}^{chloroform}$ cm^{-1}: 3500, 3420—3090, 1633. NMR δ: 4.94 and 5.20 (2H, each s, CH=C$\underline{H}_2$), 6.02 (1H, t of q, J=6, 9.5, 17.5 Hz, C$\underline{H}$=CH_2), 6.19 (1H, s, OH, D_2O exchanged), 6.61 (3H, broad s, Ar-H); (+D_2O) δ 2.77 (6H, s, 2×NMe), 3.36 (2H, s, -CH_2-), 4.96 and 5.20 (2H, each broad s, CH=C$\underline{H}_2$), 6.03 (1H, t of q, J=6, 9, 17.5 Hz, CH=C$\underline{H}_2$), 6.63 (3H, s, Ar-H). Acetate **10**, IR $\nu_{max}^{chloroform}$ cm^{-1}: 3045, 1749, 1632. NMR δ: 2.24 (3H, s, COMe), 2.89 (6H, s, 2× NMe), 3.25 (2H, d, J=6 Hz, -CH_2-), 4.95 and 5.17 (2H, m, CH=C$\underline{H}_2$), 5.96 (1H, t of q, J=6, 9.5, 17 Hz, C$\underline{H}$=CH_2), 6.60 (1H, q, J=3, 9 Hz, Ar-H), 6.58 (1H, d, J=3 Hz, Ar-H), 6.90 (1H, d, J=9 Hz, Ar-H). MS Calcd. for $C_{13}H_{12}NO_2$: 219.1259. Found: 219.1259 Hydrochloride of acetate **10**: HCl, colorless hexagonal crystal, recrystallized from acetone–ether, mp 121—131°. UV λ_{max} nm (ε): 256 (6200), 309 (900). IR ν_{max}^{KBr} cm^{-1}: 3430, 2500, 1760. NMR δ: 2.32 (3H, s, COMe), 3.22 (6H, s, 2×NMe), 3.38 (2H, d, J=6 Hz, -CH_2-), 5.02 and 5.24 (2H, m, CH=C$\underline{H}_2$), 5.95 (1H, t of q, J=6, 9, 18 Hz, C$\underline{H}$=CH_2), 7.24 (1H, d, J=9.5 Hz, Ar-H), 7.82 (1H, q, J=3, 9.5 Hz, Ar-H), 7.83 (1H, d, J=3 Hz, Ar-H). *Anal.* Calcd. for $C_{13}H_{18}ClNO_2$:C, 61.06; H, 7.09; N, 5.48; Cl, 13.86. Found: C, 60.99; H, 7.29; N, 5.68; Cl, 14.11.

Catalytic Reduction of 3-Allyl-4-acetoxy-N,N-dimethylaniline 10——Acetate **10** (174 mg) in MeOH was hydrogenated by pre-reduced Pd-$CaCO_3$ (50 mg) in hydrogen overnight. Purification on silica gel (2.5 g) with the aid of chloroform-acetone (95/5) gave liquid 3-propyl-4-acetoxy-N,N-dimethylaniline (166 mg). IR $\nu_{max}^{chloroform}$ cm^{-1}: 1750, 1206. NMR (100 MHz) δ: 0.85 (3H, t, J=7 Hz, Me), 1.51 (2H, m, -CH_2-), 2.18 (3H, s, COMe), 2.36 (2H, m, -CH_2-), 2.81 (6H, s, 2×NMe), 6.54 (1H, q, J=3, 9 Hz, Ar-H), 6.54 (1H, d, J=3 Hz, Ar-H), 6.82 (1H, d, J=9 Hz, Ar-H). MS Calcd. for $C_{13}H_{19}NO_2$: 221.1416. Found: 221.1410. Hydrochloride, colorless plate, recrystallized from acetone–ether, mp 125—140°. UV λ_{max} nm (ε): 256 (6000), 305 (1100). IR ν_{max}^{KBr} cm^{-1}: 3440, 1765. NMR δ: 0.97 (3H, t, J=7 Hz, Me), 1.67 (2H, m, -CH_2-), 2.36 (3H, s, COMe), 2.60 (2H, m, -CH_2-), 3.22 (6H, s, 2×NMe), 7.23 (1H, d, J=9.5 Hz, Ar-H), 7.73 (1H, q, J=3, 9.5 Hz, Ar-H), 7.82 (1H, s, Ar-H). *Anal.* Calcd. for $C_{13}H_{20}ClNO_2$: C, 60.61; H, 7.81; N, 5.43; Cl, 13.75. Found: C, 60.68; H, 7.61; N, 5.57; Cl, 13.69

Pyrolysis of N-Allyl-N,N-dimethylanilinium Bromide 12——a) Bromide **12** (36 g) was heated to 140° to distill in vaccum (3 mmHg), giving colorless distillate (18.50 g) and brown residue (2.26 g). Crystal in distillate was found to be starting bromide **12** (1.26 g). Distillate was then fractionally distilled in vaccum (10 mmHg) to give 10.20 g (bp—72°), 2.50 g (bp 73—89°), 1.03 g (bp 89—90°) and 1,39 g of residue. The first distillate was N,N-dimethyl-aniline and the following two fractions were a mixture of N,N-dimethylaniline **13**, N-allyl-N-methylaniline **14** and *o*-allyl-N,N-dimethylaniline **16** according to NMR and GLC analysis and their yields are 67, 10 and 6% respectively. b) Bromide **12** (16 g) was pyrolyzed in N,N-dimethylaniline (80 ml) at 145° under nitrogen overnight. Crystal appeared in reaction mixture was collected to give 12.52 g (88% yield) of N,N,N-trimethylanilinium bromide. N,N-Dimethylaniline was removed by distillation (10 mmHg). Residue was a mixtre of N,N-dimethylaniline **13** (38%), N-allyl-N-methyl-aniline **14** (45%) and 1,2-dimethylindoline **15** (17%) on GLC and distilled under 6.3 mmHg to give fraction I (3.08 g, bp—65°), 2 (1.22 g, bp 65—85°) and 3 (5.54 g, bp 84—85°). Fraction 3 was a mixture of

N-allyl-N-methylaniline **14** and 1,2-dimethylindoline **15** (70/28) and a part of which was chromatographed on silica gel (50 g) with the aid of Skellysolve B-dichloromethane to afford N-allyl-N,N-dimethylaniline **14** (692 mg) and 1,2-dimethylindoline **15** (186 mg) which was identified by IR and NMR comparisons respectively. 1,2-Di-methylindoline **15** (131 mg) was further confirmed in picrate (273 mg) by IR spectra.

Aromatic Ammonium N-Claisen Rearrangement, General Procedure——Reaction Condition A: Quaternary salt (2 mmol) in a mixture of glycerin–water (2/1, 6 ml) was heated to 140° (bath temperature) under nitrogen for 4 hr. Reaction mixture was poured into water, basified with sodium carbonate and extracted with either ether or Skellysolve B three times. Organic extract was then washed twice with saturated brine, dried on anhydrous sodium sulfate then removed solvent to give product. Reaction Condition B: Reaction as described in condition A was carried out in the presence of slightly more than equivalent amount of sodium bicarbonate. Reaction mixture was poured into brine and extracted.

Rearrangement of N-allyl-N,N-dimethylanilinium Bromide 12——Hygroscopic bromide **12** (538 mg, 2.22 mmol) in reaction condition A yielded 2-allyl-N,N-dimethylaniline **16** (211 mg) in 90% yield. Bromide **12** (530 mg, 2.19 mmol) in reaction condition B gave **16** (249 mg) in 86% purity. 2-Allyl-N,N-diemthylaniline **16**, colorless liquid, bp 83—86°/9 mmHg. IR ν_{max}^{film} cm^{-1}: 3070, 1634. NMR δ: 2.67 (6H, s, 2×NMe), 3.49 (2H, d, J=6.5 Hz, -C$\underline{H}_2$-), 4.96 and 5.18 (2H, each broad m, CH=C$\underline{H}_2$), 6.03 (1H, t of q, J=6, 9, 17.5 Hz, C$\underline{H}$=CH$_2$), 7.10 (4H, s, Ar-H). Base **16** (91 mg) was treated with ethanolic picric acid to give 160 mg of crystal which was recrystallized from chloroform-ether, giving 2-allyl-N,N-dimethyl-aniline picrate, yellow long plate, mp 143—149°. IR ν_{max}^{KBr} cm^{-1}: 3060, 2735, 1630. NMR δ: 3.36 (6H, s, 2×NMe), 3.71 (2H, d, J=6 Hz, -CH$_2$-), 4.86 and 5.12 (2H, each m, CH=C$\underline{H}_2$), 5.97 (1H, m, C$\underline{H}$=CH$_2$), 7.51 (4H, s, Ar-H). *Anal.* Calcd. for $C_{17}H_{18}N_4O_7$: C, 52.31; H, 4.65; N, 14.35. Found: C, 52.02; H, 4.55; N, 14.16.

Hydrogenation of 2-Allyl-N,N-dimethylaniline 16——Base **16** (1.161 g) was hydrogenated in MeOH (40 ml) over 5% Pd-C (0.200 g) to give colorless liquid (0.943 g) identical with 2-propyl-N,N-dimethylaniline[10] by IR and NMR comparisons. NMR δ: 0.91 (3H, t, J=7Hz, Me), 1.68 (2H, m, -CH$_2$-), 2.67 (6H, s, 2×NMe), 2.68 (2H, t, J=7 Hz, -CH$_2$-), 6.9—7.2 (4H, m, Ar-H).

Acid Cyclization of 2-Allyl-N,N-dimethylaniline 16——Olefinic base **16** (529 mg) and 37% HCl (0.422 ml was heated from 160 to 205° (bath temperature) in a period of 45 min and kept at 150° then for another 30 min. Reaction mixture was poured into brine, basified with sodium carbonate and extracted with ether to give liquid 1,2-dimethylindoline **15** (381 mg) in 98% purity.

N-Crotyl-N,N-dimethylanilinium Bromide 18——N,N-Dimethylaniline (20 g) and crotyl bromide (25 ml) in MeOH (100 ml) was stirred at 4° for 41 days. Evaporation and addition of acetone afforded 34.66 g of salt. Recrystallization from chloroform–acetone yielded N-crotyl-N,N-dimethylanilinium bromide **18**, colorless plate, mp 136.5—137.5°. IR ν_{max}^{KBr} cm^{-1}: 1655, 855. NMR δ: 1.67 (3H, d, J=7 Hz, *sec*-Me), 3.96 (6H, s, 2×NMe), 5.09 (3H, broad s, -CH$_2$- and vinyl-H), 6.25 (1H, m, vinyl-H), 7.5—8.2 (5H, m, Ar-H). *Anal.* Calcd. for $C_{12}H_{18}BrN$: C, 56.26; H, 7.08; N, 5.47; Br, 31.19. Found: C, 56.07; H, 6.85; N, 5.41; Br, 31.43.

Rearrangement of 18——Bromide **18** (5.227 g, 20.4 mmol) in reaction condition B yielded **19** (2.996 g) in 81% purity on GLC. A part of liquid was distilled at 135°/26 mmHg to give homogeneous liquid of *o-sec*-butenyl-N,N-dimethylaniline **19**, n_D^{20} 1.5206. UV λ_{max} nm (ε): 246 (4700). IR ν_{max}^{film} cm^{-1}: 3080, 2780, 1632. NMR δ: 1.20 (3H, d, J=7 Hz, *sec*-Me), 2.68 (6H, s, 2×NMe), 4.19 (1H, p, J=7 Hz, CH), 4.90 and 5.15 (2H, each, m, CH=C$\underline{H}_2$), 6.11 (1H, d of q, J=5.5, 10.0, 17.5 Hz, C$\underline{H}$=CH$_2$), 7.16 (4H, s, Ar-H). MS Calcd. for $C_{12}H_{17}N$: 175.1361. Found: 175.1358. *Anal.* Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.03; H, 10.08; N, 8.19. Picrate, recrystallized from EtOH–chloroform, mp 131—133.5°. IR ν_{max}^{KBr} cm^{-1}: 3090, 2720, 1620. NMR δ: 1.31 (3H, d, J=6.5 Hz, *sec*-Me), 3.38 (6H, s, 2×NMe), 4.13 (1H, p, J=6.5 Hz, CH), 4.88 and 5.10 (2H, each m, CH=C$\underline{H}_2$), 5.91 (1H, q, J=5.8, 10.5, 16.5 Hz, C$\underline{H}$=CH$_2$), 7.50 (4H, s, Ar-H).

***o-sec*-Butyl-N,N-diemthylaniline**——Produced by catalytic reduction of **19** over 5% Pd-C, bp 137°/36 mmHg, n_D^{20} 1.5050. UV λ_{max} nm (ε): 244.5 (4100), 280 (900). IR ν_{max}^{film} cm^{-1}: 3090, 2778. NMR δ: 0.81 (3H, t, J=7 Hz, Me), 1.18 (3H, d, J=7 Hz, *sec*-Me), 1.56 (2H, p, J=7 Hz, -CH$_2$-), 2.65 (6H, s, 2×NMe), 3.31 (1H, sex, J=7 Hz, CH), 7.13 (4H, s, Ar-H). *Anal.* Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.13; H, 10.54; N, 8.06. Picrate, recrystallized from EtOH–EtOAc-chloroform, yellow needle, mp 130—133°. IR ν_{max}^{KBr} cm^{-1}: 2760. NMR δ: 0.77 (3H, t, J=7 Hz, Me), 1.18 (3H, d, J=7 Hz, *sec*-Me), 1.62 (2H, p, J=7 Hz, -CH$_2$-), 3.21 (1H, sex, J=7 Hz, CH), 3.39 (6H, s, 2×NMe), 7.47 (4H, s, Ar-H). *Anal.* Calcd. for $C_{12}H_{19}N \cdot C_6H_3N_3O_7$: 53.20; H, 5.46; N, 13.79. Found: C, 53.38; H, 5.71; N, 13.90.

N-Isobutenyl-N,N-dimethylanilinium Chloride 20——N,N-Di-methylaniline (20.0 g) and methallyl chloride (27.16 g) in MeOH (100 ml) were left at room temperature for 41 days to give 18.31 g of salt. Recrystallization from chloroform–acetone yielded **20**, colorless plate, mp 125.5—126°. IR ν_{max}^{KBr} cm^{-1}: 3140, 1635. NMR δ: 1.27 (3H, s, Me), 4.07 (6H, s, 2×NMe), 5.20 (2H, s, -CH$_2$-), 5.33 and 5.54 (2H, each broad s, C=CH$_2$), 7.5—8.3 (4H, m, Ar-H). *Anal.* Calcd. for $C_{12}H_{18}NCl$: C, 68.07; H, 8.57; N, 6.62; Cl, 16.74. Found: C, 67.77; H, 8.55; 6.44; Cl, 16.67.

***o*-Isobutenyl-N,N-dimethylaniline 21**——Salt **20** (4.264 g) in reaction condition B gave liquid product (3.380 g) in 97% purity which was distilled to give **21**, bp 136—136°/26 mmHg, n_D^{20} 1.5235. IR ν_{max}^{film} cm^{-1}: 3063, 2775, 1637, 882. NMR δ: 1.72 (3H, s, Me), 2.67 (6H, s, 2×NMe), 3.47 (2H, broad s, -CH$_2$-), 4.85 and 4.70

(2H, each broad s, C=CH_2), 7.12 (4H, m, Ar-H). MS M^+ *m/e* 175. Picrate, recrysttallized from chloroform–EtOH, yellow plate, mp 87—98°. IR ν_{max}^{KBr} cm^{-1}: 2850, 2680, 1622. *Anal.* Calcd. for $C_{12}H_{17}N \cdot C_6H_3N_3O_7$: C, 53.46; 4.99; N, 13.85. Found: C, 53.49; H, 5.26; N, 14.14.

***o*-Isobutyl-N,N-dimethylaniline**——bp 136°/33 mmHg, n_D^{20} 1.5018. IR ν_{max}^{film} cm^{-1}: 2780. NMR δ: 0.90 (6H, d, J=6.5 Hz, 2×*sec*-Me), 1.98 (1H, sex, J=6.5 Hz, CH), 2.88 (2H, d, J=6.5 Hz, -CH_2-), 2.63 (6H, s, 2×NMe), 7.10 (4H, m, Ar-H). MS M^+ *m/e* 177. *Anal.* Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.65; H, 11.06; N, 7.64. Picrate, yellow plate from EtOH, mp 140.5—143.5°. IR ν_{max}^{KBr} cm^{-1}: 2850, 2735, 1622. *Anal.* Calcd. for $C_{12}H_{19}N \cdot C_6H_3N_3O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 52.96; H, 5.17; N, 13.53.

Rearrangement of 4-Hydroxy-N-allyl-N,N-dimethylanilinium Bromide 1——In Reaction Condition A: Bromide **1** (563 mg) in reaction condition A gave liquid product (197 mg) which was subjected to bulb-to-bulb distillation to yield 2-allyl-4-hydroxy-N,N-dimethylaniline **7**, bp 140°/0.6 mmHg. UV λ_{max} nm (ε): 238 (4500). 285 (1050). $\lambda_{max}^{MeOH+NaOH}$ nm: 244, 300. IR ν_{max}^{film} cm^{-1}: 3500, 3080, 1636. NMR δ: 2.58 (6H, s, 2×NMe), 3.39 (2H, d, J=6 Hz, -CH_2-), 4.88 and 5.11 (2H, each m, CH=CH_2), 5.47 (1H, s, OH, D_2O exchanged), 5.93 (1H, t of q, J=6.5, 9.5, 17.5 Hz, CH=CH_2), 6.70 (1H, q, J=2.5, 9.5 Hz, Ar-H), 6.70 (1H, broad s, Ar-H), 6.96 (1H, d, J=9.5 Hz, Ar-H). MS M^+ *m/e* 177. *Anal.* Calcd. $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.37; H, 8.36; N, 7.89. Acetate **9**. IR ν_{max}^{film} cm^{-1}: 3070, 1758, 1632. NMR δ: 2.23 (3H, s, COMe), 2.66 (6H, s, 2×NMe), 3.48 (2H, d, J=6.5 Hz, -CH_2-), 4.99 and 5.20 (2H, m, CH=CH_2), 6.00 (1H, t of q, J=6.5, 9.0, 17.5 Hz, CH=CH_2), 6.91 (1H, q, J=2.8, 9.5 Hz, Ar-H), 6.94 (1H, d, J=2.8 Hz, Ar-H), 7.08 (1H, d, J=9.5 Hz, Ar-H). MS Calcd. for $C_{13}H_{17}NO_2$: 219.1259. Measured: 219.1255. Picrate, yellow plate from EtOH–chloroform, mp 132.5—135°. IR ν_{max}^{KBr} cm^{-1}: 3085, 2855. NMR δ: 2.32 (3H, s, COMe), 3.31 (6H, s, 2×NMe), 3.68 (2H, d, J=6 Hz, -CH_2-), 5.00 and 5.22 (2H, each m, CH=CH_2), 5.92 (1H, t of q, J=6, 10, 16 Hz, CH=CH_2), 7.17 (1H, broad s, Ar-H), 7.27 (1H, d, J=8.5 Hz, Ar-H), 7.55 (1H, q, J=1.5, 8.5 Hz, Ar-H).

Methylation of **7**: Excess diazomethane in MeOH transformed **7** into 2-allyl-4-methoxy-N,N-dimethylaniline **26**, identified with authentic specimen prepared by rearrangement in free and picrate state on IR spectra.

In Reaction Condition B: Bromide **1** (556 mg, 2.2 mmol) in reaction condition B afforded liquid product (213 mg) which was identical on IR spectrum with steam distillation product of hydroxide **6**, consisting of **2** (8%), **8** (84%) and a new product, 3,5-diallyl-4-hydroxy-N,N-dimethylaniline **22** (8%). These products were separated on silica gel and identified both in phenol and acetate with the specimen prepared by other methods on IR spectra.

Pyrolysis of 4-Hydroxy-N-allyl-N,N-diemthylanilinium Hydroxide 6——Anilinium hydroxide **6** (IR $\nu_{max}^{chloroform}$ cm^{-1}: 3400—2300) prepared from 11.41 g of bromide **1** and silver oxide (10.336 g) in MeOH (65 ml) was heated to 210° in water-vaccum to give distillate (7.14 g) and residue (0.89 g). Distillate was fractionally distilled under 1.5—2.5 mmHg to give four fractions, fraction I (1.21 g), II (3.84 g), III (0.51 g) and residue (0.60 g). Fraction II, bp 112—114°/2.5 mmHg, was identified to be 3-allyl-4-hydroxy-N,N-dimethylaniline **8** by IR and NMR comparisons. Residue (0.60 g) was purified on silica gel (20 g) with the aid of chloroform–acetone to give 3,5-diallyl-4-hydroxy-N,N-dimethyl-aniline **22** (0.28 g). UV λ_{max} nm: 246.5. IR $\nu_{max}^{chloroform}$ cm^{-1}: 3530, 3080, 1652, 1628. NMR δ: 2.85 (6H, s, 2×NMe), 3.38 (4H, broad s, 2×-CH_2-), 4.73 (1H, s, OH, D_2O exchanged), 5.02 and 5.27 (4H, each broad s, 2×CH=CH_2), 6.06 (2H, t of q, J=6, 9, 17 Hz, 2×CH=CH_2), 6.51 (2H, s, Ar-H). MS M^+ *m/e* 217. Usual acetylation gave 3,5-diallyl-4-acetoxy-N,N-dimethylaniline which was bulb-to-bulb distilled, bp 135°/0.6 mmHg. UV λ_{max} nm: 257.5. IR $\nu_{max}^{chloroform}$ cm^{-1}: 3100, 1748. NMR (100 MHz) δ: 2.14 (3H, s, COMe), 2.79 (6H, s, 2×NMe), 3.12 (4H, t of d, J=1, 6 Hz, 2×-CH_2-), 4.91 and 5.04 (4H, each m, 2×CH=CH_2), 5.82 (2H, t of q, J=6.5, 9.5, 17.5 Hz, 2×CH=CH_2), 6.31 (2H, s, Ar-H). MS M^+ *m/e* 259.

Pyrolysis of Sodium Salt of Bromide 1——Bromide **1** (508 mg) and NaOMe (106 mg) were dissolved in MeOH and removed solvent *in vacuo*. Resulting residue was then heated to 190° to give distillate (227 mg). which was acetylated and preparatively gas-chromatographed on 20% QF-1 (10 ft by 1/4 inch) to give *p*-acetoxy-N,N-dimethylaniline (16 mg) and 3-allyl-4-acetoxy-N,N-dimethylaniline **10** (67 mg) identified by IR and GLC behaviors respectively.

4-Hydroxy-N-isobutenyl-N,N-dimethylanilinium Chloride 23——Colorless needle from MeOH–acetone, mp 163—163.5°. IR ν_{max}^{KBr} cm^{-1}: 3200—2800, 1640. NMR δ: 1.37 (3H, d, J=0.9 Hz, Me), 3.63 (6H, s, 2×NMe), 4.49 (2H, s, -CH_2-), 5.28—5.40 (2H, m, C=CH_2), 7.02 and 7.66 (4H, A_2B_2, J=9.5 Hz, Ar-H). *Anal.* Calcd. for $C_{12}H_{18}ClNO$: C, 63.29: H, 7.96; N, 6.15; Cl, 15.57. Found: C, 63.18; H, 8.17; N, 5.85: Cl, 15.81.

Rearrangement of 23——Anilinium chloride **23** (492 mg) was subjected to reaction condition A to give liquid product (100 mg) which was purified by bulb-to-bulb distillation to afford 2-isobutenyl-4-hydroxy-N,N-dimethylaniline **24**, bp 140°/0.6 mmHg. UV λ_{max} nm (ε): 288 (ε 1900). IR ν_{max}^{film} cm^{-1}: 3500—3200, 3080, 1647. NMR δ: 1.68 (3H, s, Me), 2.62 (6H, s, 2×NMe), 3.40 (2H, s, -CH_2-), 4.68 and 4.82 (2H, each m, C=CH_2), 5.86 (1H, s, OH, D_2O exchanged), 6.68 (1H, q, J=3, 9 Hz, Ar-H), 6.70 (1H, d, J=3 Hz, Ar-H), 7.06 (1H, d, J=9 Hz, Ar-H). MS Calcd. for $C_{12}H_{17}NO$: 191.1310. Measured: 191.1305. *Anal.* Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.39; H, 8.87; N, 7.31.

4-Methoxy-N-allyl-N,N-dimethylanilinium Bromide 25——mp 140—141.5° from chloroform–acetone. IR ν_{max}^{KBr} cm^{-1}: 3070, 1608. NMR δ: 3.85 (3H, s, OMe), 3.96 (6H, s, 2×NMe), 5.12 (2H, broad s, $W_{1/2}$=5 Hz,

-CH_2-), 5.2—5.7 (3H, m, CH=CH_2), 7.04 and 7.95 (4H, A_2B_2, J=9.5 Hz, Ar-H). *Anal.* Calcd. for $C_{12}H_{18}$-BrNO: C, 52.95; H, 6.66; N, 5.15; Br, 29.36. Found: C, 52.97; H, 6.88; N, 5.14; Br, 29.65.

Rearrangement of 25——Bromide **25** (545 mg, 2.0 mmol) in reaction condition A yielded liquid **26** (214 mg) in 94% purity. IR ν_{max}^{film} cm^{-1}: 3080, 1636. NMR δ: 2.64 (6H, s, 2×NMe), 3.50 (2H, d, J=6.5 Hz, -CH_2-), 3.77 (3H, s, OMe), 4.99 and 5.22 (2H, each m, C=CH_2), 6.06 (1H, t of q, J=6.5, 9.5, 17.5 Hz, C<u>H</u>=CH_2), 6.71 (1H, q, J=3, 8 Hz, Ar-H), 6.84 (1H, d, J=3 Hz, Ar-H), 7.12 (1H, d, J=8 Hz, Ar-H). Picrate, yellow rod from EtOH, mp 138.5—140.5°. IR ν_{max}^{KBr} cm^{-1}: 3050, 1620. NMR δ: 3.30 (6H, s, 2×NMe), 3.60 (2H, d, J=6 Hz, -CH_2-), 3.83 (3H, s, OMe), 4.97 and 5.18 (2H, each m, CH=C<u>H</u>$_2$), 5.91 (1H, m, C<u>H</u>=CH_2), 6.8—7.6 (3H, m, Ar-H). *Anal.* Calcd. for $C_{12}H_{17}NO \cdot C_6H_3N_3O_7$: C, 51.43; H, 4.80; N, 13.38. Found: C, 51.23; H, 4.82; N, 13.56. In reaction condition B 581 mg of **25** gave 256 mg of liquid product identical with that obtained in reaction condition A by IR comparison.

***p*-Hydroxy-N-allyl-N,N-dimethylanilinium Chloride**——Bromide **1** (3.27 g) was treated with silver oxide (4.00 g) in MeOH (20 ml) overnight. Inorganic precipitate was removed and filtrate was acidified with 37% HCl (1.26 ml) under cooling. Reaction mixture was then evaporated and residue was recrystallized from MeOH–chloroform–acetone to give chloride, colorless rod, mp 158—162.5°. IR ν_{max}^{KBr} cm^{-1}: 3200—2500, 1637. *Anal.* Calcd. for $C_{11}H_{16}ClNO$: C, 61.82; H, 7.55; N, 6.55; Cl, 16.59. Found: 61.74; H, 7.65; N, 6.38; Cl, 61.63.

***p*-Hydroxy-N-allyl-N,N-dimethylanilinium Iodide**——*p*-Dimethyl-aminophenol (2.02 g) was allylated with allyliodide (3.1 g) in MeOH (65 ml) to give 2.79 g of crystal which was recrystallized from MeOH–acetone–ether to give iodide, colorless rod, mp 138.5—140.5° IR ν_{max}^{KBr} cm^{-1}: 3160, 1612. *Anal.* Calcd. for $C_{11}H_{16}INO$: C, 43.30; H, 5.29; N, 4.59; I, 41.58. Found: C, 43.37; H, 5.36; N, 4.51; I, 41.71.

***p*-Methoxy-N-allyl-N,N-dimethylanilinium Chloride**——N,N-Dimethyl-*p*-anisidine (1.70 g) was refluxed with allychloride (20 ml) in MeOH (50 ml) in the presence of molecular seave type 4A for 17 hr to give 2.361 g of crystal which was recrystallized from chloroform–acetone to give hygroscopic chloride, mp 153° (dec.). IR ν_{max}^{KBr} cm^{-1}: 1640. *Anal.* Calcd. for $C_{12}H_{18}ClNO$: C, 62.06; H, 8.25; N, 6.03; Cl, 15.26. Found: C, 62.34; H, 7.98; N, 6.31; C., 15.21.

***p*-Methoxy-N-allyl-N,N-dimethylanilinium Iodide**——N,N-Dimethul-*p*-anisidine (1.76 g) and allyliodide (2.8 g) in ether gave 3.58 g of salt which was recrystallized from chloroform–acetone–EtOAc to give iodide, colorless rod, mp 122—124°. IR ν_{max}^{KBr} cm^{-1}: 3105, 1600. *Anal.* Calcd. for $C_{12}H_{18}INO$: C, 45.16; H, 5.68; N, 4.39; I, 39.76. Found: C, 45.14; H, 5.79: N, 4.21: I, 39.89.

N-Allyl-N,N-dimethylanilinium Tetrafluoroborate——Bromide **12** (2.40 g) was dissolved in water (20 ml) into which was dropped sodium tetrafluoroborate (5.0 g) in water (10 ml), leading to red oil isolation. Extraction with methylenechloride gave red oily tettrafluoroborate (2.13 g). IR ν_{max}^{film} cm^{-1}: 3630, 3570, 1635. NMR (DMSO-d_6) δ: 3.55 (6H, s, 2×NMe), 4.48 (2H, d, J=5 Hz, -CH_2), 5.48 (3H, m, CH=CH_2), 7.4—8.0 (5H, m, Ar-H).

Rearrangement of N-Allyl-N,N-dimethylanilinium Tetraphenylborate——Tetraphenylborate[5] (968 mg, 2.0 mmol) in dry DMF was heated in a sealed tube at 142° for 5.5 hr. Reaction mixture was poured into brine, basified with M-Na_2CO_3 and extracted with ether, giving three layer. Ether layer was collected and extraction was repeated three times. Lower two layers were extracted with methylenechloride two times. Ether and methylenechloride extracts were washed, dried on anhydrous sodium sulfate and removed solvent to give liquid (477 mg) and solid product (269 mg) respectively. Liquid product was separated into basic (288 mg) and neutral (188 mg) parts. Basic part was a mixture of N,N-dimethylaniline (10%) and *o*-allyl-N,N-dimethylaniline **16** (88%) on GLC and transferred into picrate to identify.

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