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Treatment of 1,1-dimethyl-2-tolylpiperidinium halides with sodium amide in liquid ammonia affords derivatives of 2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine *via* the Sommelet-Hauser rearrangement. Structures of the reaction products have been established by ^{13}C nmr. In the case of 1,1-dimethyl-2-benzylpiperidinium halide, only an elimination reaction takes place.

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Ammonium ylides may isomerise by three different pathways: α',β elimination, Stevens rearrangement (1,2 migration) and Sommelet-Hauser rearrangement (2,3 migration) (1). All processes can occur simultaneously under certain conditions but when the ylide is $\beta\text{-}\gamma$ unsaturated with respect to nitrogen atom, the latter is favoured when the base system is sodium amide in liquid ammonia. Pyrrolidinium and piperidinium salts may be involved in enlargement of a five- or six-membered ring to an eight- or nine-membered ring, respectively (2,3). Ring expansions of ammonium or sulfonium ylides by 2,3-sigmatropic shifts have been studied elsewhere (4,5).

By the workup described by Lednicer and Hauser (3a), 1,1-dimethyl-2-tolylpiperidinium halides **1a-c** afford the derivatives of 2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine **2a-c** in good yields. The reaction is selective with *o*- and *p*-tolylpiperidinium salts, but three compounds are obtained with the *meta*-isomer. 1,1-Dimethyl-2-benzylpiperidinium chloride **1d** gives only one elimination product. Pure samples of benzazonine were obtained by distillation, followed by pgpc in the case of **2b** and **2b'**. Results are summarized in Table I.

The structure of compounds **2a-c** have been determined by ^{13}C nmr starting from 2-methyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine **2e** (3a). In this product, the lines of aromatic carbons can be assigned by comparison

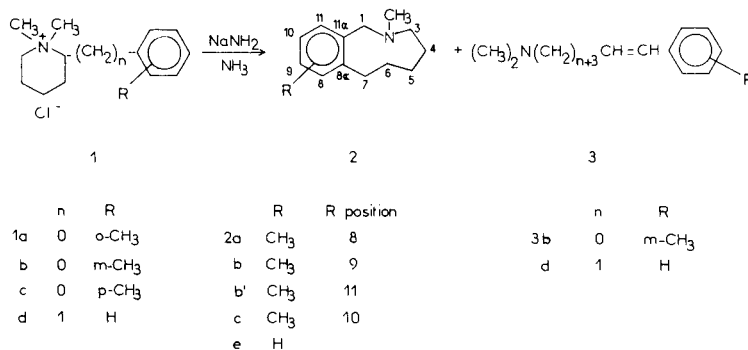
of data of the free base and its methiodide **4e** on the one hand, and calculated shifts of the amine on the other hand [obtained with chemical shift differences between *N*-dimethylbenzylamine and its quaternary ammonium (6)] (see Table II). Experimental increments are in good agreement with data of **2c** and its methiodide **4c** (Table III).

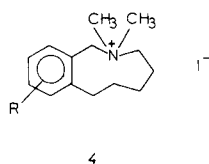
Substituent effects (6) in benzenes are approximately additive unless substituents are *ortho* with respect to each other (7). The calculated values agree with data for **2b** and **2c** (see Table III) but in the case of **2a** and **2b'**, some differences appear. The methyl group substituted on the aromatic ring shields C-7 (in **2a**) or C-1 (in **2b'**); these upfield shifts arise from steric interactions between hydrogens of the methyl group and those of the *ortho*

Table I

Products Obtained by Treatment of **1** with Sodium Amide

Starting Material	Yield %	Composition %	
		2	3
1a	87	100	0
1b	93	42 of 2b + 54 of 2b'	4
1c	89	100	0
1d	84	0	(48.5% <i>E</i> and 51.5% <i>Z</i>)





	R	R position
4a	CH ₃	8
b	CH ₃	9
b'	CH ₃	11
c	CH ₃	10
e	H	

carbon (8). Sharp lines of doublets of C-10 (in **2a**) or C-9 (in **2b'**) display the lack of 3J (C,H) couplings, stronger in benzenic ring than 2J (C,H) and 4J (C,H) (7).

The signal multiplicity in off-resonance or under-coupled spectra allows to distinguish easily primary, secondary, tertiary and quaternary carbons. The chemical shifts of C-4, C-5, C-6 and C-7 cannot be assigned unambiguously and have not been reported. Results are summarized in Table IV.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Glc analysis and purifications were carried out on a Girdel 3000 instrument using columns packed with 15% Carbowax 20M and 5% potassium hydroxide on 60-80 mesh chromosorb P. Mass spectra were performed in mode EI on a Ribier R 10 10 instrument. All new compounds **2a-c** exhibit the molecular ion 203.

1H nmr spectra were recorded on a Varian A 60 A instrument.

Table II

Chemical Shifts of Aromatic Carbons of **2e** and **4e**

Compound No.	Solvent		δ C-8a	δ C-8	δ C-9	δ C-10	δ C-11	δ C-11a
4e	dimethyl sulfoxide- <i>d</i> ₆		146.2	131.2	130.8	126.0	133.9	126.0
2e	deuteriochloroform	Calcd. (a)	141.8	129.6	126.5	124.4	129.5	136.7
		Found	143.4	130.2	127.3	125.3	129.6	138.3
$\Delta\delta$ (4e-2e)			+2.8	+1.0	+3.5	+0.7	+4.3	-12.3

(a) Starting from chemical shifts of **4e** and from increments arising from dimethylbenzylamine and its quaternary ammonium (6).

Table III

Chemical Shifts of Aromatic Carbons of **2b**, **2c** and **4c**

Compound No.	Solvent		δ C-8a	δ C-8	δ C-9	δ C-10	δ C-11	δ C-11a
2c	none	Calcd. (a)	140.4	130.1	128.0	134.5	130.3	138.2
		Found	141.0	131.1	128.9	134.9	131.1	138.7
4c	dimethyl sulfoxide- <i>d</i> ₆	Calcd. (b)	143.8	132.1	132.4	135.6	135.4	126.4
		Calcd. (c)	143.2	131.1	131.5	135.2	134.6	125.9
		Found	143.3	131.3	131.7	135.3	134.4	125.9
2b	carbon tetrachloride	Calcd. (a)	143.3	130.9	136.5	126.0	129.5	135.3
		Found	143.9	131.9	137.1	126.9	130.5	135.9

(a) Starting from chemical shifts of **2e** and from increments arising from benzene and toluene (6). (b) Starting from chemical shifts of **2c** and from increments of Table II. (c) Starting from chemical shifts of **4e** and from increments arising from benzene and toluene (6).

Table IV

^{13}C Chemical Shifts of Compounds **2**

Compound No.	Solvent	δ N-CH ₃	δ Ar-CH ₃	δ C-1	δ C-3	δ C-8	δ C-8a	δ C-9	δ C-10	δ C-11	δ C-11a
2c	none	44.9	21.9	62.8	55.9	131.1	141.0	128.9	134.9	131.1	138.7
2b	carbon tetrachloride	44.9	22.1	62.5	55.9	131.9	143.9	137.1	126.9	130.5	135.9
2a	none	44.2	20.5	63.3	54.9	139.1	142.1	130.3	126.0	128.6	137.3
2b'	carbon tetrachloride	44.4	21.7	56.3	54.3	129.4	144.7	127.9	129.0	137.1	137.3
				or 54.3	or 56.3	or 129.0		or 129.4	or 137.3	or 137.1	

The natural abundance ^{13}C nmr spectra were obtained by Fourier transformation carried out on a Bruker WP 60 spectrometer at 15.08 MHz, a Bruker WP 80 at 20.15 MHz and a Perkin-Elmer R32 at 22.63 MHz. The products were examined in 10 mm tubes in pure liquid state (or as solutions in carbon tetrachloride) with external lock, or in deuteriochloroform (or dimethyl sulfoxide- d_6) solutions as internal lock signal. Usually a spectral width of 3500-4000 Hz was used with 8192 memory points and with a flip angle of 20-25°. Tetramethylsilane was used as an internal reference of chemical shifts (in ppm). All spectra were recorded at room temperature.

Typical Procedure for Quaternary Ammonium Halide (**1a-d**) Rearrangements.

In a 1 l. three necked flask equipped with a mechanical stirrer, a cooled methanol condenser and a thermometer, a small piece of clean sodium metal is added to 350 ml. of commercial anhydrous liquid ammonia. After the appearance of a blue color, a few crystals of hydrated ferric nitrate are added, where upon the blue color is discharged. The remainder of the 4.6 g. (0.2 gram atom) of sodium is then rapidly added as small pieces. After all the sodium has been converted to sodium amide, 0.1 mole of the solid quaternary ammonium halide is added over a period of ten minutes. The resulting red-brown reaction mixture became gray during a two additional hours stirring and then neutralized with 0.2 mole of solid ammonium chloride. The residue which remained after the ammonia had evaporated is washed with water and extracted with ether. The organic layer is dried over potassium carbonate. The oil which remained when the solvent is removed is distilled *in vacuo* to afford the amine. Further purification by fractional distillation and preparative vapor phase chromatography is achieved in the case of the products obtained from ammonium **1b** and **1d**.

Compounds **1** and **3** were reported in previous papers (9,10).

2,8-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2-benzazone (**2a**).

This compound was obtained in a yield of 87%, b.p. 139° (9 mm), $n_{\text{D}}^{23} = 1.5399$; nmr (carbon tetrachloride): δ 6.8-7 (3H, m, 9-H, 10-H, 11-H), 3.60 (2H, s, 1-H), 2.95 (2H, t, 7-H), 2.36 (3H, s, Ar-CH₃), 2.30 (3H, s, N-CH₃), 2-2.57 (2H, m, 3-H), 0.9-2.0 (6H, m, 4-H, 5-H, 6-H).

Anal. Calcd. for C₁₄H₂₁N: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.35; H, 10.44; N, 6.84.

2,9-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2-benzazone (**2b**).

This compound was obtained in a yield of 39%, b.p. 142° (11 mm), $n_{\text{D}}^{23} = 1.5367$; nmr (carbon tetrachloride): δ 6.75-

6.97 (3H, m, 8-H, 10-H, 11-H), 3.58 (2H, s, 1-H), 2.90 (2H, t, 7-H), 2.35 (3H, s, Ar-CH₃), 2.27 (3H, s, N-CH₃), 2.13-2.57 (2H, m, 3-H), 1.1-2.03 (6H, m, 4-H, 5-H, 6-H).

Anal. Calcd. for C₁₄H₂₁N: C, 82.70; H, 10.41; N, 6.89. Found: C, 83.18; H, 10.32; N, 6.82.

2,11-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2-benzazone (**2b'**).

This compound was obtained in a yield of 50%, b.p. 143-144° (11 mm), $n_{\text{D}}^{23} = 1.5405$; nmr (carbon tetrachloride): δ 6.80-7.12 (3H, m, 8-H, 9-H, 10-H), 3.69 (2H, s, 1-H), 2.87 (2H, t, 7-H), 2.40 (3H, s, Ar-CH₃), 2.32 (3H, s, N-CH₃), 2.1-2.5 (2H, m, 3-H), 1.12-2 (6H, m, 4-H, 5-H, 6-H).

Anal. Calcd. for C₁₄H₂₁N: C, 82.70; H, 10.41; N, 6.89. Found: C, 83.05; H, 10.37; N, 6.84.

2,10-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2-benzazone (**2c**).

This compound was obtained in a yield of 89%, b.p. 141-142° (10 mm), $n_{\text{D}}^{23} = 1.5355$; nmr (carbon tetrachloride): δ 6.93-7.18 (3H, m, 8-H, 9-H, 11-H), 3.67 (2H, s, 1-H), 3.00 (2H, t, 7-H), 2.37 (3H, s, Ar-CH₃), 2.27 (3H, s, N-CH₃), 2.17-2.63 (2H, m, 3-H), 1.15-2.05 (6H, m, 4-H, 5-H, 6-H).

Anal. Calcd. for C₁₄H₂₁N: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.74; H, 10.42; N, 6.91.

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