A Convenient Synthesis of *o*-Methylbenzylamine Derivatives from Benzyl Halides: The Improved Sommelet–Hauser Rearrangement

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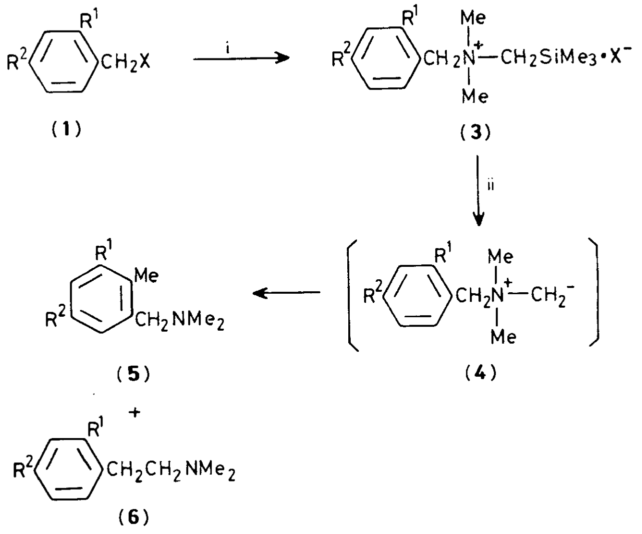
Desilylation by fluoride anion of benzyldimethyl(trimethylsilylmethyl)ammonium halides having a Cl^-, CN^-, or AcO^- substituent on the benzene ring gave high yields of the Sommelet–Hauser rearrangement products at room temperature.

The applicability of the Sommelet–Hauser rearrangement to benzyl quaternary ammonium salts often provides a useful synthetic sequence to *ortho*-alkyl-substituted benzylamine derivatives.[1] Since this rearrangement is usually carried out using strong bases, such as $NaNH_2$ in liquid NH_3, if a substituent on the benzene ring prevents formation of the required ylide intermediate, rearrangement will not occur. Halogen substituents appear to decrease markedly the yield of rearrangement product, apparently by side reactions.[2] The treatment of *p*-cyanobenzylammonium salts did not give rearrangement products but led to the recovery of the starting materials.[3]

Earlier papers dealing with the reaction of benzyldimethyl(triorganosilylmethyl)ammonium halides with $LiAlH_4$ or $NaNH_2$ reported the participation of cleavage of the carbon–silicon bonds to give ammonium ylide intermediates (**4**).[4] This result suggests that the employment of fluoride anion should provide a new route to the Sommelet–Hauser rearrangement in a neutral medium.

Benzyldimethyl(trimethylsilylmethyl)ammonium halides (**3**) were prepared by reaction of the corresponding benzyl halide derivatives (**1**) with (dimethylaminomethyl)trimethylsilane (**2**). A solution of (**3**) (2 mmol) and caesium fluoride (10 mmol) in hexamethylphosphoramide (10 ml) was stirred at room temperature, and the mixture was worked up in the usual manner. The results are summarized in Table 1.

Satisfactory yields of the Sommelet–Hauser rearrangement products (**5**) were obtained from all reactions. The contamination by the competing Stevens rearrangement products,



Scheme 1. i, $Me_3SiCH_2NMe_2$ (**2**), Me_2CO; ii, CsF, (KI), hexamethylphosphoramide, room temperature.

Table 1. Reaction of benzyldimethyl(trimethylsilylmethyl)ammonium halides (**3**) with caesium fluoride.

Run	(**3**)	R^1	R^2	X	Reaction time (h)	% Yield[a] (**5**)	(**6**)
1	**a**	H	H	Cl	44	28.4	0.4
2	**a**	H	H	Cl[b]	20	74.1	0.6
3	**b**	H	H	Br	15	81.8	2.2
4	**c**	Me	H	Br	25	80.0	3.7
5	**d**	H	Me	Br	25	73.3	3.3
6	**e**	Cl	H	Cl[b]	25	65.0	4.1
7	**f**	H	Cl	Cl[b]	23	83.9	0.4
8	**g**	H	CN	Br	25	71.0	16.8
9	**h**	H	OAc	Br	22	69.8	2.1

[a] Overall yields are of the isolated mixed products, the ratios were determined by g.l.c. analysis (10% PEG-20M). [b] The reaction was carried out in the presence of KI.

N,*N*-dimethyl-2-phenylethylamine derivatives (**6**), is quite low in this reaction, except for the *p*-cyano derivative (**3g**). The rate of the reaction of the chloride (run 1) was slower than that of the bromide (run 3), but it was accelerated by addition of KI (6 mmol) in the reaction mixture (run 2). Thus this reaction proceeds in a neutral medium at room temperature, and applies to compounds having a halogeno, cyano, or acetoxy substituent on the phenyl group.

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