A New Rearrangement of Dialkylmethyl(2-triphenylsilylethyl)ammonium Ylides

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Summary Treatment of dialkylmethyl(2-triphenylsilylethyl)ammonium halides (**1a**—**c**) with n-butyl-lithium gave the corresponding (dialkylaminomethyl)triphenylsilanes (**2a**—**c**) *via* the formation of ylides (**6a**—**c**).

THREE types of base-promoted reactions of quaternary ammonium salts are well known;[1] the Stevens rearrangement, the Sommelet–Hauser rearrangement, and the Hofmann elimination. The present paper reports a new

Table. Yields (%) of products

	R^1	R^2	X	(**2**)	(**3**)	(**4**)	(**5**)	(**1**) (recovery)
a	Me	Me	I	50·9(56·5)	15·9(17·2)	1·1(1·3)	1·9(2·1)	9·9
b	Et	Et	Br	7·4(15·5)	30·5(63·8)	0·4(0·9)	—	52·2
c	Me	Pr^{i}	I	8·3(14·4)	41·8(72·7)	1·9(3·2)	—	42·7
d	Me	**Ph**	**I**	—	89·6	1·0	—	—

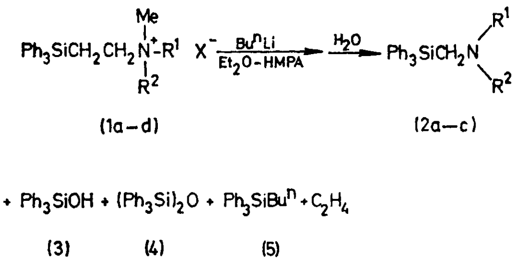
Yields in parentheses based on unrecovered (**1**).

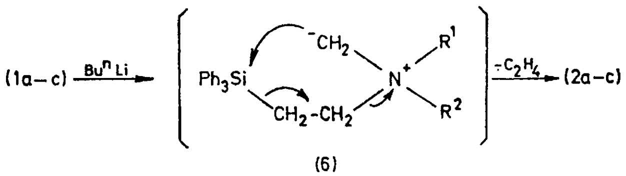
rearrangement of β-triphenylsilylethylammonium ylides (**6**) to triphenylsilylmethylamines (**2**).

When a small excess of n-butyl-lithium was added to a chilled (−15° to −25°) solution of trimethyl(2-triphenylsilylethyl)ammonium iodide (**1a**) in ether–hexamethylphosphoramide (HMPA), a red colour appeared and then disappeared after a few seconds. Treatment of this reaction mixture gave (dimethylaminomethyl)triphenylsilane (**2a**), triphenylsilanol (**3**), hexaphenyldisiloxane (**4**), and n-butyltriphenylsilane (**5**), besides (**1a**). A similar reaction of diethylmethyl(2-triphenylsilylethyl)ammonium bromide (**1b**) or dimethylisopropyl(2-triphenylsilylethyl)-ammonium iodide (**1c**) with n-butyl-lithium led to (diethylaminomethyl)triphenylsilane (**2b**) or (methylisopropylaminomethyl)triphenylsilane (**2c**), accompanied by (**3**), respectively.

In all cases the silylmethylamines (**2a**—**c**)† were the sole basic products and none of the Stevens 1,2-shift products could be detected. The formation of the silylmethylamines (**2a**—**c**) from the silylethylamines (**1a**—**c**) is thought to result from nucleophilic attack of the intermediate carbanions (**6a**—**c**) on the triphenylsilyl unit followed by elimination of ethylene.

Reaction of dimethylphenyl(2-triphenylsilylethyl)ammonium iodide (**1d**) with n-butyl-lithium, however, gave *NN*-dimethylaniline (63·6%), (**3**) (89·6%), (**4**) (1·0%), and no (methylphenylaminomethyl)triphenylsilane expected from the results described above.





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† Satisfactory analytical results were obtained for all new compounds.

[1] S. H. Pine, 'Org. Reactions,' Wiley, New York, 1970, vol. 18, p. 403.