New Rearrangement in the Reaction of (Dimethylaminomethyl)-phenylsilanes with Benzyne

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Summary When (dimethylaminomethyl)phenylsilanes (**1a—c**) are treated with benzyne the corresponding benzyl (*o*-dimethylaminophenyl)diorganosilanes (**2a—c**) and 1-(methylphenylamino)ethylphenylsilanes (**3a—c**) are produced.

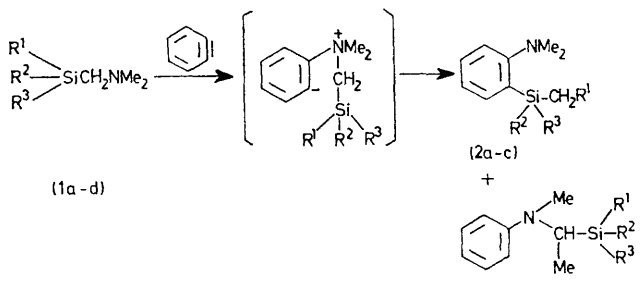
IT is well known[1] that benzyne reacts with tertiary amines to form ylide intermediates which subsequently rearrange *via* Stevens and/or Sommelet-Hauser pathways. The reaction of (dimethylaminomethyl)trimethylsilane (**1d**) with benzyne gave predominantly 1-(methylphenylamino)ethyltrimethylsilane (**3d**) (the Stevens rearrangement product).[2]

In the cases of (dimethylaminomethyl)triorganosilanes (**1a**), (**1b**), and (**1c**) having at least one phenyl substituent on the silicon, the Stevens rearrangement competed with a novel rearrangement involving migration of a silyl group to

TABLE. Yields of products/%

	R^1	R^2	R^3	(2)	(3)	(1) (recovery)
(a)	Ph	Ph	Ph	8·7(13·8)[a]	4·5(7·2)	37·2
(b)	Ph	Ph	Me	12·7(23·6)	7·8(14·6)	45·7
(c)	Ph	Me	Me	10·8(16·6)	11·1(17·2)	35·4
(d)	Me	Me	Me	—	60·0	—

[a] Yields in parentheses based on unrecovered (1).



the benzene ring accompanied by the shift of a phenyl group from the silicon to the adjacent carbon. The reactions were carried out by addition of bromobenzene to a boiling suspension of (**1a**), (**1b**), or (**1c**) and sodium amide in tetrahydrofuran. The structures of the new rearrangement products, the benzyl(*o*-dimethylaminophenyl)diorganosilanes (**2a**), (**2b**), and (**2c**), were confirmed by spectral comparison with authentic samples prepared from *o*-bromo-*NN*-dimethylaniline and the corresponding benzylchlorosilanes.

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[1] A. R. Lepley and A. G. Giumanini, 'Mechanisms of Molecular Migrations,' Wiley, New York, 1971, vol. 3, p. 394.
[2] Y. Sato, T. Aoyama, and H. Shirai, *J. Organometallic Chem.*, 1974, **82**, 21.