Single-atom Peri-bridged Naphthalenes; 1,1-Dialkylnaphtho[1,8-*bc*]siletes

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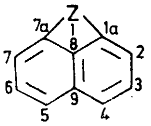
Summary Reactions of 1,1-dialkyldichlorosilanes with 1,8-dilithionaphthalene yield 1,1-dialkylnaphtho[1,8-*bc*]-siletes.

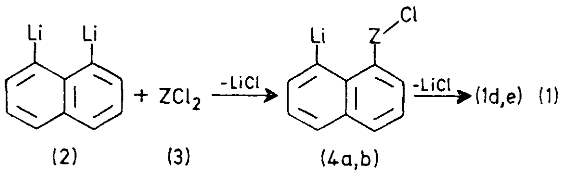
Naphthalenes connected in the *peri*-positions by sulphur or carbon single-atom bridges have been prepared by photolytic extrusion methods. Thus compounds (**1a**),[1] (**1b**),[2] and (**1c**)[3] are produced upon irradiation of naphtho-[1,8-*de*][1,2,3]-thiadiazine 1,1-dioxide, naphtho[1,8-*cd*][1,2]-dithiole 1,1-dioxide, and (8-bromo-1-naphthyl)diazomethane respectively. We now report that 1,8-dilithionaphthalene (**2**) reacts readily with diethyl- (**3a**) and dimethyl-dichlorosilane (**3b**) to give the naphtho[1,8-*bc*]siletes (**1d**) and (**1e**), respectively. The present method of synthesis of the *peri*-silicon-bridged naphthalenes (**1d** and **e**) presumably involves successive displacements as indicated in equation (1) and is convenient and efficient experimentally.



(**1**)

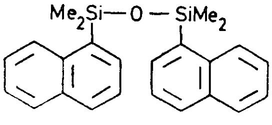
a, Z = SO_2
b, Z = S
c, Z = CHBr
d, Z = Et_2Si
e, Z = Me_2Si

It has thus been found that slow addition of (**3a**) in Et_2O to (**2**)[4] (prepared from Bu^nLi and 1,8-dibromonaphthalene or 1,8-di-iodonaphthalene in Et_2O) at 0 °C followed by vacuum distillation and preparative gas chromatography of the products gives (**1d**) ($\gg$43%) as a colourless oil. The silete (**1d**)† can be handled without serious difficulty in oxygen-free, anhydrous environments. Its structure is assigned as (**1d**) on the basis of its physical properties, analysis, molecular weight, and chemical origin: b.p. 80 °C at 0·02 mmHg; *m/e* 212·10221 (M^+); *M* (osmometry, $CHCl_3$) 210; δ ($CDCl_3$, Me_4Si) 1·06 (10H, m, Et) and 7·45—7·85 (6H, m, ArH); δ (^{13}C) 7·12 (Me), 7·55 (CH_2) 125·04 (C-2 and -7), 126·39 (C-4 and -5), 127·55 (C-9), 128·14 (C-3 and -6), and 143·33 (C-1a and -7a) p.p.m.; ν_{max} 3040, 2960, 2870, 1475, 1150, 1000, 850, and 785 cm^{-1}. The u.v. properties of (**1d**) are similar to that of naphthalene and 1*H*-cyclobuta[*de*]naphthalene.[3]



a, Z = Et_2Si
b, Z = Me_2Si

The silete (**1e**)† is obtained ($\gg$25%) by reaction of (**2**) and (**3b**) at 0 °C, distillation, and gas chromatography; b.p. 65 °C at 0·04 mmHg; *m/e* 184 (M^+). (**1e**) is somewhat less stable in air and moisture than is (**1d**). Hydrolysis of (**1e**) occurs readily with cleavage of the silicon bridge to give the disiloxan (**5**), *m/e* 386 (M^+).



(**5**)

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† Satisfactory elemental analyses were obtained.

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