

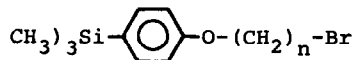
ORGANOSILICON COMPOUNDS X. TRIMETHYLSILYL-ARYL ETHERS AS  
REACTION INTERMEDIATES

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We recently became interested in preparing some p-trimethylsilylphenoxy-alkylbromides (I) to be utilized in work being conducted in these laboratories (1,2).

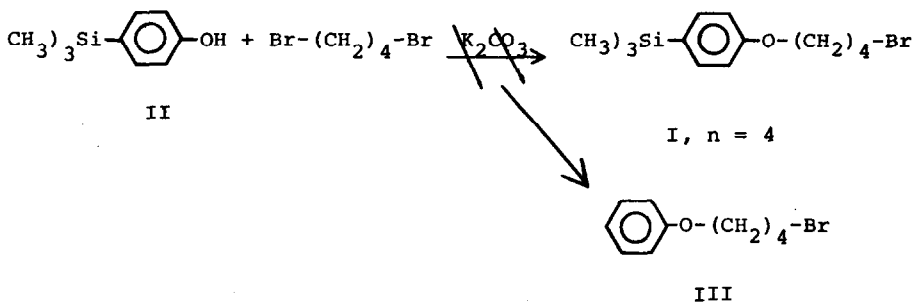


I

where n = 2, 3, 4, etc.

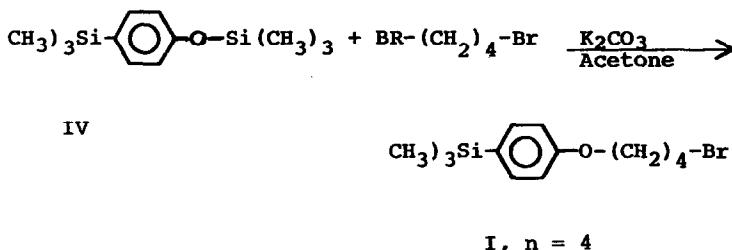
Our initial efforts towards the production of I, n = 4, which involved the reaction of p-trimethylsilylphenol (II) (3,4,5) with the appropriate alkyl dibromide, were unsuccessful (Scheme I) in that silicon-aryl bond cleavage, as well as ether formation, occurred to provide a 91% yield of 4-bromobutylphenyl ether (III) (6).

Scheme I



It was felt that the difficulties associated with such a procedure could be related to the inherent instability of p-trimethylsilylphenol (4). In order to circumvent these difficulties, a novel approach was successfully executed with the reaction of 1-trimethylsilyl-4-trimethylsiloxybenzene (IV) with 1,4-dibromobutane and potassium carbonate in acetone (Scheme II), to provide a 67% yield of I,  $n = 4$ , (b.p.  $124^{\circ}/0.45$  mm.,  $n_D^{27} = 1.5247$ ) after an 18 hour reflux period.

Scheme II



Previously we had synthesized methyl-4-methylthio-3-methylphenoxyacetate (V), (b. p.  $110^{\circ}/0.025$  mm.,  $n_D^{25} 1.5591$ ) and methyl-4-methylthiophenoxyacetate (VI), (b. p.  $105^{\circ}/0.005$  mm.,  $n_D^{25} 1.5612$ ) in 67 and 52% yields, respectively, via reaction of the corresponding phenols with methyl bromoacetate and potassium carbonate in refluxing acetone for 96 hrs. Since we envisioned the displacement of the trimethylsilyl group from trimethylsilylaryl ethers as a new and general facile preparative sequence for the synthesis of ethers, we felt that the preparation of V and VI by this method would be noteworthy.

To this end, 4-methylthio-3-methylphenoxytrimethyl silane (VII) and 4-methylthiophenoxytrimethylsilane (VIII) were reacted with methyl bromoacetate and potassium carbonate in refluxing acetone for 6 hrs. affording V in a 74% yield and VI in a 45% yield. However, in the case of VI we also obtained a 22% yield of 4-methylthiophenoxyacetic acid, presumably as a result of the base catalyzed cleavage of VI. Thus, in the cases reported, this technique provides comparable if not superior yields of desired products concomitant

with a reduction in reaction time.

To our knowledge this represents the first report of ether formation via a siloxane intermediate. The high yields obtained and the nature of this method suggests this reaction to be a promising, general synthetic procedure. The scope and limitations of this method are being investigated in these laboratories and will be the subject of a later communication.

Satisfactory elemental analysis and infrared spectra have been obtained for all the new compounds mentioned above.

The compound, 1-trimethylsilyl-4-trimethylsiloxybenzene (IV), was prepared in the manner described by Neville (4) utilizing the Grignard reagent prepared from p-bromophenoxy trimethylsilane (IX). Compound IX, previously synthesized by other workers (3-5) utilizing the chlorosilane, was prepared by heating p-bromophenol and hexamethyldisilazane without solvent at 50° for 2 hrs. in 97% yield. The reaction between phenols and hexamethyldisilazane has been described by Langer, *et. al.* (7).

The preparation of VII (b. p. 115°/ 1.5 mm.,  $n_D^{25}$  1.5267) and VIII (b. p. 105°/ 1.5 mm.,  $n_D^{25}$  1.5263) was accomplished in 92 and 90% yields, respectively, from hexamethyldisilazane and the corresponding phenol as described for the preparation of IX.

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