

Aromatic Substitution by Trimethylsilyl Radicals

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SUBSTITUTED silyl radicals can displace halogen atoms¹ or other substituted silyl groups² from aromatic rings, but there has been no clear example of displacement of hydrogen from aromatic rings by such radicals in reactions analogous to free radical alkylations, although some reactions at high temperatures may involve such displacements. (For example, homolytic dissociation of the Si-H bond could be the initiating step in the formation of phenyltrichlorosilane from trichlorosilane and benzene in the vapour phase at 600–850° or the liquid phase under pressure at 350–500°.³) We now report evidence for such substitution involving trimethylsilyl radicals generated by photolysis of bis(trimethylsilyl)mercury.

Thus, when a *ca.* 0.5 M solution of bis(trimethylsilyl)mercury in anisole at room temperature is exposed to light from a Hanovia medium pressure mercury arc (Type U.V.S. 500/A), the products, in addition to hexamethyldisilane, formed in *ca.* 50% yield, include *o*-, *m*-, and *p*-trimethylsilylanisole in *ca.* 8, 4, and 1% yield, respectively. Similarly,

toluene gives *o*-, *m*-, and *p*-trimethylsilyltoluene in roughly 2:2:1 ratio, and benzene gives phenyltrimethylsilane in *ca.* 21% yield. Mercury is formed quantitatively in each case, and no significant reaction occurs in the absence of light. The isomer distributions are consistent with free-radical substitution.

The reaction under thermal activation between the mercurial and anisole at 185° takes mainly a very different course, the major product being phenoxytrimethylsilane, which is formed in a direct molecular interaction,⁴ not in a radical process as was tentatively suggested.⁵ Trimethylsilyl radicals probably also have a less important role than previously thought in the thermal interaction of (trimethylsilyl)mercury and halogenobenzenes,⁵ and it is now clear that photolysis of the mercurial⁶ provides a more satisfactory source of these radicals than pyrolysis.

(Received, June 27th, 1967; Com. 657.)

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