Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

Methylation of tetrakis(trichlorosilyl)allene

Tetrakis(trichlorosilyl)allene (I) has been obtained in an interesting study by Müller and Beyer[1] as one of the products from the direct synthesis using carbon tetrachloride and silicon–copper alloy, and also from the dechlorination with copper powder of bis(trichlorosilyl)dichloromethane (an intermediate in the direct synthesis).

The dodecamethyl analog of (I), tetrakis(trimethylsilyl)allene (II), has been shown in this laboratory[2] to be a product of reaction of certain polyhalobenzenes and trimethylsilyl-substituted polyhalobenzenes (notably hexachlorobenzene) with excess lithium and chlorotrimethylsilane in tetrahydrofuran. The allene, (II), was also obtained earlier by West and co-workers[3] in a splendid study, in addition to 1,3,3-tris(trimethylsilyl)propyne by treatment of tetralithiopropyne with chlorotrimethylsilane. Compound (II) has now been obtained from (I) by methylation with methyllithium:

$$\underset{\text{(I)}}{(Cl_3Si)_2C{=}C{=}C(SiCl_3)_2} \xrightarrow{12\ \text{MeLi}} \underset{\text{(II)}}{(Me_3Si)_2C{=}C{=}C(SiMe_3)_2}$$

Apropos the facile opening of the polychlorophenyl nucleus, the observations were made[2] that the allene was detected (VPC) when a first aliquot was removed at the end of five minutes from the reaction starting with (pentachlorophenyl)trimethylsilane and also with 1,4-bis(trimethylsilyl)tetrachlorobenzene. In subsequent studies concerned with the scope and mechanisms of such reactions, we have observed that these two polychlorophenyl compounds showed the formation of allene when aliquots were removed at the end of one minute. Furthermore, hexachlorobenzene also showed the formation of allene at the end of one minute.

Addition of methyllithium (0.2 mole, excess) in ether to a solution of (I) (5.74 g, 0.01 mole) in tetrahydrofuran (100 ml) at $-78°$ showed no apparent reaction; vapor phase chromatography confirmed the absence of (II) at low temperatures. On warming to ambient temperatures, a precipitate of lithium chloride formed and VPC indicated the presence of (II) in the reaction mixture. After stirring for 3 h, the excess of methyllithium was destroyed by addition of chlorotrimethylsilane until Color Test I[4] was negative. Workup and distillation of the product using a semimicro Nester–Faust spinning-band column gave tetrakis(trimethylsilyl)allene (II), b.p. 60–62°/0.1 mm, n_D^{20} 1.4770 (0.88 g, 26.8%) (lit.[2] values: b.p. 69–70°/0.2 mm., n_D^{20} 1.4770). The infrared spectrum of the product was identical with that of authentic (II) showing characteristic silicon–methyl and allenic bands at 1246 and 1880 cm^{-1}, respectively.

Acknowledgements

This research was supported in part by the United States Air Force under Contract AF 33(615-2368 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. We are grateful to Prof. Richard Müller for providing us with a sample of his tetrakis(trichlorosilyl)allene.

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Received June 12th, 1967