The Reaction of Silicon Monoxide with Toluene and Iodine

William N. Rowlands and Peter L. Timms

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

In a novel reaction, condensing SiO gas attacks toluene very efficiently in the presence of iodine at −90 °C to give a polysiloxane oil with 2- and 4-$C_6H_4CH_3$, I and H as substituents; oily polyiodosiloxanes are made from SiO and I_2 in iodoethane solution at −110 °C.

Gaseous silicon monoxide SiO, has been much less used in chemical synthesis than other divalent silicon compounds such as SiF_2, $SiCl_2$ or SiR_2.[1,2] A previous study indicated that SiO will react with aromatic and other unsaturated organic compounds, but that the products are intractable solid polysiloxanes in which both addition to multiple C–C bonds and insertion in C–H bonds has occurred.[3]

In an effort to make the previously unknown polyiodosiloxanes, $(I_2SiO)_n$, we condensed SiO vapour (*ca.* 90 mmol) (generated from Merck 'Silicon Monoxide' at 1300 °C) into a solution of I_2 (47 mmol) in toluene (300 cm^3) at −90 °C under vacuum in a rotary solution reactor.[4] The final light brown and almost clear solution was filtered and evaporated to yield a very moisture sensitive, colourless, viscous oil. The i.r., mass and ^{1}H, ^{13}C and ^{29}Si n.m.r. spectra of the product showed it to be a polysiloxane with tolyl, iodo and hydrogen substituents on silicon.

In the electron impact m.s. of the product using a heated probe the high mass ions were mainly of type $[(SiO)_n(C_7H_7)_mI_k]^+$ where $n = 3$—5, $m = 2$—3 and $k = 2n - m - 1$. The ^{29}Si n.m.r. spectrum showed six broad resonances of roughly equal intensity at δ −73.5, −76.0, −86.0, −91.7, −97.5 and −167.0 p.p.m. and a weaker resonance at −241.5 p.p.m. The resonance at −86.0 p.p.m. was split into a doublet in the ^{1}H coupled spectrum ($^1J_{Si-H}$ 317 Hz); further evidence for a Si–H group was obtained from the broad resonance at δ 4.74 in the ^{1}H spectrum and the band at 2260 cm^{-1} in the i.r. spectrum.

We believe that the seven resonances in the ^{29}Si n.m.r. spectrum are associated with the following five types of moieties each of which is sharing its oxygen atoms with adjacent silicon atoms: (a) $(C_6H_4CH_3)SiO_{1.5}$, −73.5, −76.0 p.p.m.; (b) $HSiO_{1.5}$, −86.0 p.p.m.; (c) $(C_6H_4CH_3)ISiO$, −91.7, −97.5 p.p.m.; (d) I_2SiO, −167.0 p.p.m.; (e) $I_3SiO_{0.5}$, −241.5 p.p.m.

Our assignments of (d) and (e) are based on the ^{29}Si n.m.r. spectrum of the poly(iodosiloxane) described below. The assignment of two resonances each to groups type (a) and (c) assumes that these groups each occur in two different environments, *e.g.* in siloxane rings and chains or in rings of different sizes.[5]

Chemical analysis and the C–H : Si–H ratio determined by ^{1}H n.m.r. spectroscopy, are consistent with a ratio of O : Si : I : C_7H_7 : H of 24 : 20 : 17 : 11 : 4. Treatment of the product with D_2O yielded deuterio-toluenes; about 82% 2-deuterio-toluene and 4-deuterio-toluene, 10% dideuterio-toluenes, 8% 3-deuterio-toluene, but no $C_6H_5CH_2D$, *i.e.* only aromatic hydrogen atoms were substituted by SiO, with a marked preference for attack on the *ortho*- and *para*-positions. This result contrasts with deuteriolysis of the toluene-insoluble product we obtained by condensing SiO into toluene at −90 °C in the absence of iodine; this gave mostly methyl substituted dideuteriocyclohexa-1,4-dienes, in line with earlier results on SiO and benzene,[3] but also some $C_6H_5CH_2D$.

Treatment of the product with diethyl ether at low temperatures caused replacement of Si–I by Si–OEt. The ethoxylated product is an oil with a molecular weight (osmometry) of 2300. The ^{29}Si n.m.r. spectrum suggests that the ethoxylated product is structurally closely related to the iodo-product, although we cannot be sure that cleavage was completely avoided as the reaction with ether was very exothermic. The spectrum showed six resonances, three little changed from the iodo-product at δ −71.1 and −72.8 p.p.m. [corresponding to group (a)] and at −86.1 p.p.m. [corresponding to group (b)]; new resonances at δ −62.5, −62.8 and −96.4 p.p.m. are thought to correspond to OEt/I exchange on groups (c) and (d) respectively. No peak corresponding to $(EtO)_3SiO$ was seen but it may be coincident with the broad peak at −86.0 p.p.m.

We obtained colourless, oily polyiodosiloxanes by condensing SiO into a solution of iodine in iodoethane at −110 °C. The ^{29}Si n.m.r. spectrum of the product was complex with about twenty resonances in three regions, −148.9 to −157.3 ($ISiO_{1.5}$), −166.7 to −175.4 (I_2SiO), and −238.6 to −245.4 p.p.m. ($I_3SiO_{0.5}$). However, the mass spectrum of the oil was dominated by peaks of type $Si_3O_3I_n^+$ (n = 3, 5 and 6), indicating release of $Si_3O_3I_6$ on heating. Condensing SiO into a solution of iodine in iodoethane containing about 10% of cumene or 1-methylnaphthalene, resulted in the formation mainly of polyiodosiloxanes. Deuteriolysis of the products showed that aromatic substitution (but not attack on the methyl groups) had occurred to a small extent, especially with 1-methylnaphthalene.

The mechanism by which toluene undergoes aromatic substitution in its reaction with SiO and iodine is not obvious. The absence of substitution on the methyl group of toluene seems to rule out attack by $\ddot{\mathrm{S}}\mathrm{iO}$ or by $\mathrm{I\dot{S}iO}$. It is possible that an electrophile such as $\mathrm{ISiO^+}$ is produced from free I_2 and that this attacks the toluene solvent. Perhaps more likely, SiO reacts with I_2 molecules complexed between toluene molecules[6] and this leads to a concerted electrophilic attack on the toluene and release of HI. Part of the HI may be captured by reaction with more SiO giving the observed SiH bonds in the product; as no HISiO moiety is seen in the product, disproportionation to give $\mathrm{HSiO_{1.5}}$ and $\mathrm{I_3SiO_{0.5}}$ moieties may occur.

Our results have revealed a new type of aromatic substitution reaction by a silylene which is an efficient way of making silicon–aryl bonds. It is possible that iodine will also modify the reactivity of other silylenes towards aromatic hydrocarbons and this is being investigated.

We thank Elkem Materials and the S.E.R.C. for a CASE studentship and for research support.

Received, 20th June 1989; Com. 9/02616I

References

1 C. Liu and T. Hwang, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 1.
2 G. R. Gillette, G. H. Noren, and R. West, *Organometallics*, 1989, **8**, 487.
3 E. T. Schaschel and P. L. Timms, *J. Organomet. Chem.*, 1972, **35**, 69.
4 P. L. Timms, 'Cryochemistry,' eds. M. Moskovits and G. A. Ozin, Wiley, New York, 1976, p. 129.
5 E. A. Williams, *Annu. Rep. N.M.R. Spectrosc.*, 1983, **15**, 235.
6 A. J. Downs and C. J. Adams, 'Comprehensive Inorganic Chemistry,' vol. 2, eds. J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon, 1973, p. 1196.