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PRELIMINARY NOTE

The cleavage of tetraphenylsilane by Raney nickel

Raney nickel catalysts have been used frequently to hydrogenate organic groups bonded to silicon[1]. A relevant example[2] is the preparation of tetracyclohexylsilane by the hydrogenation of tetraphenylsilane in the presence of W-7 Raney nickel at 100° and 60–100 atm.

We have found that tetraphenylsilane reacts with excess Raney nickel at atmospheric pressure and at temperatures between *ca.* 20° and 101° to give benzene and cyclohexane. Thus, a solution of tetraphenylsilane (0.018 mole) in boiling dioxane (200 ml; containing *ca.* 10% methanol) was treated for four hours with W-7 Raney nickel[3] (prepared from 125 g of 1:1 nickel–aluminium alloy; washed first with methanol and then with dioxane) to give 17% benzene and 49% cyclohexane*. The same quantity of catalyst reacted with 0.015 mole of tetraphenylsilane at room temperature during 48 hours to give 35% benzene and 2% cyclohexane*; 60% of the silane was recovered. Catalysts containing less hydrogen (*e.g.*, W-1 Raney nickel[4]) gave more benzene and less cyclohexane without lowering the total yield of these hydrocarbons, indicating that the primary product of the hydrogenolysis of tetraphenylsilane was benzene. By-products isolated in yields below 1% include biphenyl, triphenylsilanol, and tetracyclohexylsilane. The fate of the silicon atom in this reaction has not been determined, but *ca.* 50% of the silicon introduced as silane was found in the residue left after digestion of the spent catalyst with hydrochloric acid**. Silicon hydrides were not detected*, but in view of the alkaline nature of the catalyst (*cf.* ref. 3) this was not to be expected[5].

We have also measured the poisoning coefficient[6] of tetraphenylsilane[7] (0.11) and conclude that chemisorption of this compound occurs mainly via the silicon atom, as for electronic[8] and steric reasons adsorption involving one of the phenyl groups should be less favoured than, for example in triphenylamine (poisoning co-

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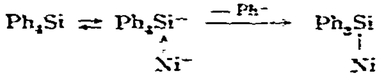
* Determined by gas chromatography using a 12-feet column packed with B.D.S. (10%) on gaschrom P.

** This determination was carried out by Dr. K. Norrish with a vacuum fluorescent X-ray spectrograph on a sample fused in lithium borate glass.

efficient[7] 0.022), which reacts with W-7 Raney nickel under similar conditions to give mainly hydrogenated products and only a little benzene[7]. In the absence of lone electrons or suitably occupied *d*-orbitals[9] we envisage chemisorption of tetraphenylsilane to occur mainly by dative bonding from the catalyst to the silicon atom. The resulting species (I) may be stabilised either by desorption or by expulsion of an anion to give (II). One factor which may influence the balance between these processes is the stability of the leaving anion, and this may explain why tetracyclohexylsilane and cyclohexyltrimethylsilane are unaffected by W-7 Raney nickel while phenyltrimethylsilane yields benzene, cyclohexane, methane and a little cyclohexyltrimethylsilane*.



$$\mathrm{Ph_4Si} \rightleftharpoons \underset{\underset{\mathrm{Ni^-}}{\uparrow}}{\mathrm{Ph_4Si^-}} \xrightarrow{-\mathrm{Ph^-}} \underset{\underset{\mathrm{Ni}}{|}}{\mathrm{Ph_3Si}}$$

(I) (II)

The intermediate (II) is thought to undergo hydrogenolysis by mechanisms analogous to those operating in hydrogenolyses such as the Raney nickel desulphurisation[10]. The formation of some biphenyl in the hydrogenolysis of tetraphenylsilane is compatible with this view (*cf.* ref. 11).

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* Determined by gas chromatography using a 12-feet column packed with B.D.S. (10%) on gaschrom P.

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