the conditions of the transmercuration reaction. A four-centre type process involving the mercury atom as the electrophile and the phenyl group as the proton acceptor therefore seems more plausible. Thus, the data for fluorobenzene and biphenyl suggest that the primary step (1) leads to the usual *para–ortho*-isomer patterns of electrophilic substitution; subsequently, these patterns change as a result of equilibration (2).

The present findings strongly suggest that the discrepancies often observed[4,5,6] in direct mercurations carried out in non-aqueous systems—*e.g.* by means of mercuric acetate—are at least partly due to transmercuration–equilibration reactions (2) following the formation of the arylmercury acetates. (*Cf.* the data given in the last two rows of the table.)

Kinetic as well as preparative studies on these new reactions are in hand in this Laboratory.

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Received March 18th, 1965

J. Organometal. Chem., 3 (1965) 487–489

The tetraalkylammoniumhalide-catalyzed redistribution of hydrogen and chlorine on silicon

The redistribution of ligands attached to silicon offers a synthetic route to many organochlorosilicon hydrides. Of particular use and interest are catalysts which allow redistribution of silanic hydrogen and chlorine without altering the carbon ligands attached to silicon[1]. Whitmore, Pietrusa, and Sommer[2] found that aluminum chloride, under mild conditions, favored hydrogen–chlorine exchange.

$$Et_3SiH + Et_2SiCl_2 \longrightarrow Et_3SiCl + Et_2SiHCl + Et_2SiH_2$$

Dolgov, Voronkov, and Borisov[3,4,5] and Gilbert, Cooper, and Shade[6] later used this method in the synthesis of organomonochlorosilanes and organodichlorosilanes. As aluminum chloride is also an effective catalyst for the redistribution of silanic hydrogen with alkyl or aryl groups[7], careful control of catalyst concentration and temperature is required to avoid complicating side reactions[3,4,6]. Isomerization of alkyl groups with aluminum chloride has also been noted[5].

A number of nitrogen bases, including dialkylcyanamides and nitriles, were shown by Bailey, Wagner, and Shafer[8] to be more specific catalysts for the redistribution of hydrogen and chlorine on silicon.

$$MeHSiCl_2 \underset{100°C}{\overset{R_2NCN}{\rightleftharpoons}} MeH_2SiCl + MeSiCl_3$$

This method has been used by Petrov, Ponomarenko, and Odabashyan[9,10] and by Petrov and Vdovin[11] who added pyridine to the list of catalysts. Studies in our laboratory have shown amides and tertiary phosphines to also be effective in promoting these exchanges. Unfortunately, none of the above Lewis base catalysts will give hydrogen–chlorine redistribution on silanes bearing more than one organo substituent. We now wish to report the use of tetraalkylammonium halides as uniquely effective and more general catalysts for the silanic hydrogen–halogen exchange in organochlorosilanes and the use of this reaction for the preparation of organodichlorosilanes from organotrichlorosilanes.

A redistribution of silanic hydrogen and chlorine occurs on contacting a variety of organochlorosilicon hydrides with 1% tetrabutylammonium chloride at 25 to 100°. Some representative examples of this reaction are shown in Table 1. Unlike the oxygen and nitrogen bases, this halide ion catalyst is quite effective in the redistribution of silanic hydrogen and chlorine in diorganochlorosilanes. These exchanges, however, were considerably slower than those involving monoorganochlorosilanes. Tetrabutylammonium chloride was equally effective in promoting the transfer of silanic hydrogen from triorganosilanes to organotrichlorosilanes.

$$R_3SiH + R'SiCl_3 \rightleftharpoons R_3SiCl + R'HSiCl_2$$

Tetrabutylphosphonium chloride was found to be qualitatively equivalent to tetrabutylammonium chloride in several of the reactions in Table 1. Tetrabutylammonium bromide and iodide will catalyze this ligand redistribution, but are less effective than the chloride under equivalent conditions.

In none of the experiments in Table 1 did the v.p.c. or ^1H NMR analyses show any products indicative of alkyl or aryl redistributions. However, trace amounts of silane have been noted in preparative scale experiments with phenyldichlorosilane which would require either cleavage or transfer of an aryl group.

The ability to transfer hydrogen between a greater variety of silicon atoms has provided a better picture of the equilibria in these hydrogen–halogen redistributions. As with many other ligand redistributions on silicon[12,13] these reactions do not give the distribution of products predicted from a random arrangement of exchanging ligands. This preliminary study suggests the following rules for qualitatively predicting the direction of these deviations from random distributions.

(*a*) The combination of products giving the most equal distribution of chlorine among the several silicon atoms will be favored.

(*b*) The combination of products placing the hydrogen on the silicon atom bearing the least number of organic substituents will be favored.

By both of these generalizations the triorganosilanes and diorganomonochlorosilanes are effective reagents for the conversion of organotrichlorosilanes to organodichlorosilanes. In fact, as seen from Table 1, these conversions were nearly quantitative

TABLE 1

REDISTRIBUTION OF HYDROGEN AND CHLORINE ON SILICON

Reactants[a]	*Conditions*[b]	*Products*[c]	
$HSiCl_3$	25°, 1 h[d]	$SiCl_4$ (0.11–0.14)	H_2SiCl_2 (0.11–0.14)
$MeHSiCl_2$	100°, 1 h[d]	$MeSiCl_3$ (0.14–0.18)	MeH_2SiCl (0.11–0.18)
Me_2HSiCl	100°, 6 h[d]	Me_2SiCl_2 (0.17–0.20)	Me_2SiH_2 (0.17–0.20)
$MeHSiCl_2$(1.0) Me_2HSiCl(1.0)	100°, 20 h[d]	Me_2SiCl_2 (0.64) $MeSiH_3$ (0.14)	MeH_2SiCl (0.42) $MeSiCl_3$ (0.06)
$PhMe_2SiH$ (1.0) $MeSiCl_3$ (1.0)	100°, 24 h[d]	$MeHSiCl_2$ (0.76) MeH_2SiCl (0.16)	$PhMe_2SiCl$ (> 0.92)
$PhSiCl_3$ (1.0) $PhSiH_3$ (1.0)	100°, 18 h[d]	PhH_2SiCl (0.33)	$PhHSiCl_2$ (0.52)
Me_2HSiCl (1.0) $PhSiCl_3$ (2.0)	Reflux, 24 h[e,g]	Me_2SiCl_2 (> 0.90)	$PhHSiCl_2$ (0.65)[f]
Me_2HSiCl (1.0) $CF_3CH_2CH_2SiCl_3$ (1.5)	Reflux, 24 h[e]	Me_2SiCl_2 (> 0.90)	$CF_3CH_2CH_2SiHCl_2$ (0.81)[f]

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[a] Molar ratio of reactants given in parentheses. [b] Tetrabutylammonium chloride was used at 1% concentration in the preparative experiments and at approximately 0.5 to 1.5% concentration in the smaller scale experiments. [c] The moles of product per mole of initial silicon hydride are given in parentheses. These product ratios were obtained by v.p.c. analyses and by integration of the various ^1H NMR absorptions for methyl and hydrogen on silicon. These amounts of the various products did not change on further heating or on increasing the catalyst concentration and thus approximate the distribution of silanes at equilibrium. [d] Approximately 0.5 ml of the reactants were heated in sealed NMR sample tubes. [e] Molar quantities of the reactants were heated at reflux (50–85°) in a flask equipped with a dry ice condenser. [f] V.p.c. analyses showed a nearly quantitative conversion to the indicated products. After the addition of ferric chloride (1.5 mole per mole of catalyst) the molar quantities of organodichlorosilane shown in the parentheses were isolated by fractional distillation. [g] Caution! Trace amounts of silane have been detected in the vent gases from this reaction and detonations have occurred during reactions which were not conducted under nitrogen!

by v.p.c. analyses and up to 80% yields of organodichlorosilane were isolated in preparative experiments.

$$Me_2HSiCl + RSiCl_3 \rightleftharpoons Me_2SiCl_2 + RHSiCl_2$$

Also, as predicted from the second generalization, the organodichlorosilane can be converted to organomonochlorosilane by further reaction with dialkylchlorosilane.

$$Me_2HSiCl + RHSiCl_2 \rightleftharpoons Me_2SiCl_2 + RH_2SiCl$$

The high yields reported by previous workers[2,4,5] in the reduction of alkyltrichlorosilanes and dialkyldichlorosilanes with triethylsilane are in accord with the above generalizations. Further studies on these equilibria are in progress.

The decreasing reactivity of the silanes with increasing alkyl substitution on the silicon suggests a mechanism involving nucleophilic attack at the silicon atom, presumably by the halide ion.

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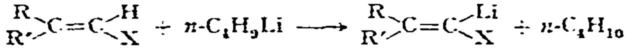
Received March 8th, 1965

J. Organometal. Chem., 3 (1965) 489–492

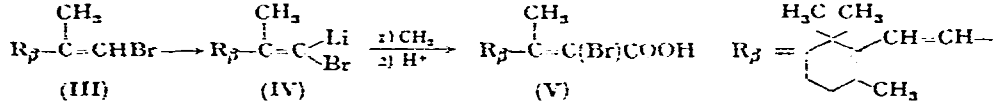
Stabile α-Bromvinyllithium-Derivate*

Die kürzlich gelungene Darstellung etlicher α-Chlorvinyllithium-Verbindungen (Ia) durch Metallierung der entsprechenden Chlorolefine (II) bei tiefer Temperatur in Tetrahydrofuran[1–3] veranlasste uns zur Untersuchung der Frage, ob die entsprechenden, voraussichtlich weniger stabilen Bromderivate (Ib) auf ähnlichem Wege zugänglich sind.



(II) (Ia): X = Cl; (Ib): X = Br

Wir fanden, dass das bereits früher aus β-Jonon und Brommethylentriphenylphosphoran in guter Ausbeute erhaltene[4] β-Jonylidenbrommethan (III) unter den üblichen[1–3] Bedingungen bei —95° in die zugehörige Lithiumverbindung (IV) übergeht, wie die bei nachfolgender Carboxylierung erhaltene Carbonsäure vom Schmp. 116° anzeigt, die auf Grund des Syntheseweges und physikalischer Daten [λ_{max} 291 mμ, log ε 4.04 (in Methanol)] 1-Brom-1-β-jonylidenessigsäure (V) darstellt. Die relativ geringe Ausbeute von 24% d.Th. führen wir vorbehaltlich einer eingehenderen Prüfung auf den allgemein bei Verbindung des Typs $>C<^{H}_{Br}$ mit alkalimetallorganischen Verbindungen bevorzugten Halogen-Metallaustausch[5] zum halogen-



(III) (IV) (V)

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[*] 7. Mitteilung über Kohlenstoffatome mit Halogen- und Alkalimetall-Substituenten. Für 6. Mitteilung siehe Ref. 1.