THE REACTION OF HALOMETHYLZINC HALIDES WITH TRIETHYLSILANE

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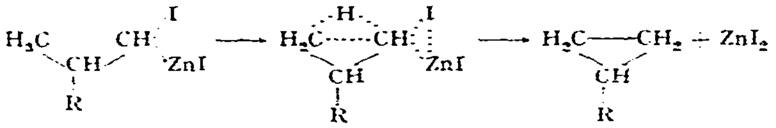
Halomethylzinc compounds, XCH_2ZnX and $Zn(CH_2X)_2$, transfer CH_2 to olefins to give cyclopropanes. The available evidence indicates that a direct reaction between the zinc reagent and the olefin is occurring[1]. To date only two reports of insertion of CH_2 into C–H bonds using such reagents have appeared. Reactions of monosubstituted acetylenes with iodomethylzinc iodide have been shown to occur in moderate yield[2], *e.g.*,

$$ICH_2ZnI + C_6H_5C{\equiv}CH \longrightarrow C_6H_5C{\equiv}CCH_3\ (29\%) + ZnI_2$$

Cyclopropane formation during reaction of $CH_3CH_2CHI_2$ and $(CH_3)_2CHCHI_2$ with the zinc–copper couple was interpreted as occurring as follows:



If concerted C–Zn cleavage and 1,3-hydride shift takes place, then this reaction can be regarded as an intramolecular insertion of a ZnI_2-complexed carbene into a C–H linkage[3].

In our studies of halomethylmercury compounds we have found CX_2, CHX and CH_2 insertion into the Si–H bond (via $BrCX_2$–Hg, BrCHX–Hg and ICH_2–Hg reagents) to occur much more readily in higher yield and with fewer side reactions than insertion into the C–H bond[4]. This prompted us to investigate the reaction of the halomethylzinc halides with triethylsilane.

This study has shown that both iodomethylzinc iodide and bromomethylzinc bromide react with triethylsilane to give triethylmethylsilane in good yield.

$$(C_2H_5)_3SiH + XCH_2ZnX \xrightarrow{Et_2O} \begin{array}{l} (C_2H_5)_3SiCH_3 + ZnX_2 \\ (64\%,\ X = I) \\ (55\%,\ X = Br) \end{array}$$

The reactivity of trialkylsilanes toward halomethylzinc halide was compared with that of olefins. When five molar equivalents each of tri-*n*-butylsilane and cyclo-

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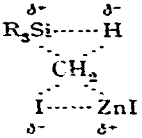
hexene were allowed to compete for the iodomethylzinc iodide prepared from one molar equivalent of methylene iodide, tri-*n*-butylmethylsilane and bicyclo[4.1.0]-heptane were formed in yields of 51.5% and 2.3% respectively. In view of the relatively narrow spread of relative reactivities of olefins toward iodomethylzinc iodide[1d], trialkylsilanes appear to be much more reactive than even the most reactive olefins.

The mechanism of this new insertion reaction is not known. The polar character of the Si–H bond, $>\!\mathrm{Si}^{\delta+}\!-\!\mathrm{H}^{\delta-}$, makes a direct insertion reaction via transition state (I) seem feasible.


(I)

However, a reduction–alkylation sequence:

$$\mathrm{R_3SiH + XCH_2ZnX \longrightarrow R_3SiX + CH_3ZnX}$$
$$\mathrm{R_3SiX + CH_3ZnX \longrightarrow R_3SiCH_3 + ZnX_2}$$

or an alkylation–reduction sequence:

$$\mathrm{R_3SiH + XCH_2ZnX \longrightarrow XCH_2SiR_3 + HZnX}$$
$$\mathrm{XCH_2SiR_3 + HZnX \longrightarrow R_3SiCH_3 + ZnX_2}$$

also are possibilities, and further experiments are required to resolve this question. A mechanism involving free methylene is not considered probable in view of the work of Simmons *et al.*[1a,d,e] on $\mathrm{ICH_2ZnI}$–olefin reactions.

Incidental to these studies it was found that sodium trichloroacetate can be used to insert dichlorocarbene into the Si–H bond of triethylsilane. The yield of

$$\mathrm{Cl_3CCOONa \longrightarrow NaCl + CO_2 + CCl_2 \xrightarrow{R_3SiH} R_3SiCCl_2H}$$

(dichloromethyl)triethylsilane obtained, however, was much lower than that obtained in the $\mathrm{(C_2H_5)_3SiH/C_6H_5HgCCl_2Br}$ reaction[4a].

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Triethyl- and tri-*n*-butylsilane were purchased from Peninsular Chem. Research, Inc.

Reaction of $BrCH_2ZnBr$ with triethylsilane

A zinc-copper couple (0.2 g-atom of zinc) was prepared by the method of Le Goff[5]. The ether-moist, freshly prepared couple was used immediately in the flask in which it was prepared. Anhydrous ether (40 ml) was added and a small amount of methylene bromide, and the mixture was heated to reflux. The remaining methylene bromide (28.0 g, 0.16 mole total) was mixed with 11.6 g (0.1 mole) of triethylsilane and 10 ml of ether. This solution was added dropwise to the couple with stirring and refluxing. The reaction mixture was heated at reflux for 48 h, then cooled to room temperature. The ether solution was decanted carefully from the unreacted Zn/Cu couple and was treated with ice and 1 N HCl, washed with water and dried over anhydrous potassium carbonate. The ether was removed by distillation. The residue was distilled *in vacuo* into a receiver at −78°, and the resulting clear distillate was analyzed by gas chromatography (g.l.c.) using a 20% General Electric Co. SE-30 Gum on Chromosorb W column (jacket at 100°, preheater at 120°, 15 psi He). Ethylbenzene was used as internal standard in the yield determination. The yield of triethylmethylsilane was 55%. A sample was isolated by preparative g.l.c. Its infrared spectrum and refractive index (n_D^{25} 1.4152) were in good agreement with those reported by Westermark[6].

Reaction of ICH_2ZnI with triethylsilane

A mixture of 10.7 g (0.04 mole) of methylene iodide and 30 mg iodine was added to a mixture of 3.27 g (containing *ca.* 0.05 g-atom of zinc) of Zn/Cu couple[7] and 35 ml of anhydrous ether. The mixture was stirred at reflux for 30 min. Triethylsilane (11.6 g, 0.1 mole) in 30 ml of ether was added to the refluxing mixture over a 30 min period. The reaction mixture was heated at reflux for a total of 44 h. Several g.l.c. probes indicated that the peak corresponding to triethylmethylsilane did not increase after one day at reflux. The yield determination via g.l.c. showed that triethylmethylsilane had been formed in 64% yield. The reaction mixture was filtered from 0.58 g of black solid. The filtrate was treated with alcoholic silver nitrate (to remove unreacted silane) and then trap-to-trap distilled *in vacuo*. The distillate was concentrated using a Widmer column, and a sample of triethylmethylsilane, identical in all respects with an authentic sample, was isolated by preparative g.l.c.

Competition of tri-n-butylsilane and cyclohexene for iodomethylzinc iodide

Essentially the procedure described above was used in the competition reaction involving the Zn/Cu couple (from 0.14 g-atom of zinc, prepared by the method of Le Goff[5]), 0.03 mole of methylene iodide, 0.15 mole each of tri-*n*-butylsilane and cyclohexene, in 50 ml of diethyl ether at reflux for 48 h. The filtered, hydrolyzed, distilled and concentrated organic phase was treated with alcoholic silver nitrate solution. The organic products were extracted with ether, and the ethereal extracts were dried and analyzed using an F & M Model 700 Gas Chromatograph (temperature range 95–200° at 10° per sec, 30 psi helium, SE-30 column). Ethylbenzene was used as standard, and it was determined that tri-*n*-butylmethylsilane had been formed in 53% yield, norcarane in 2.3% yield. Another such reaction was carried out on one-half this scale: tri-*n*-butylmethylsilane: 50%; norcarane: 2.2%.

Norcarane was identified by comparing its infrared spectrum and refractive index (n_D^{25} 1.4538) with those of an authentic sample. The same procedure was used to identify tri-*n*-butylmethylsilane. An authentic sample was prepared by the reaction of methyllithium with tri-*n*-butylsilane in ether–THF. Its infrared spectrum agreed with that reported by Westermark[6] and its refractive index (n_D^{20} 1.4382) with that reported by Arbuzov and Vinogradova[8] (n_D^{20} 1.4375).

Insertion of dichlorocarbene into triethylsilane via sodium trichloroacetate

Sodium trichloroacetate (3.7 g, 0.02 mole) was dried for 20 h at 100° *in vacuo* and then suspended in 75 ml of 1,2-dimethoxyethane which had been dried over potassium. Triethylsilane (7 g, 0.06 mole) was added slowly with stirring and the mixture was heated at reflux under nitrogen for 21 h. The reaction mixture was cooled and filtered to remove 1.2 g of sodium chloride. The filtrate was distilled *in vacuo* into a receiver at −78°. The clear, colorless distillate was analyzed by g.l.c. (SE-30 column, jacket at 180°, 15 psi helium, ethylbenzene standard). The yield of (dichloromethyl)triethylsilane was 32%. A sample was isolated by preparative g.l.c.; its infrared spectrum and refractive index were identical with those of an authentic sample prepared by Burlitch[4a]. A similar reaction carried out for 6 h gave $(C_2H_5)_3SiCCl_2H$ in 21% yield.

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SUMMARY

The action of halomethylzinc halides on trialkylsilanes results in insertion of CH_2 into the Si–H bond to give trialkylmethylsilanes in good yield. Trialkylsilanes are more reactive toward halomethylzinc halides than are olefins. The insertion of dichlorocarbene into the Si–H bond of triethylsilane using sodium trichloroacetate as CCl_2 source is described.

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