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AN IMPROVED CYCLIZATION PROCEDURE FOR 3-CHLOROPROPYL-CHLOROSILANES: EFFICIENT SYNTHESES OF SILACYCLOBUTANES

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SUMMARY

Powdered magnesium activated by 1,2-dibromoethane has proved to be an efficient agent for cyclizing (3-chloropropyl)chlorosilanes to silacyclobutanes. 1,1-Dichlorosilacyclobutane, 1-chloro-1-methylsilacyclobutane, 1,1-dimethylsilacyclobutane, and 4-silaspiro[3,3]heptane have been prepared in yields greater than 75%. Discussion of synthetic routes to the precursors of the spiro compound are also included.

GENERAL DISCUSSION

A number of methods have been used to effect the transformation of (3-halopropyl)halosilanes to silacyclobutanes[1]. All of these involve the use of magnesium as

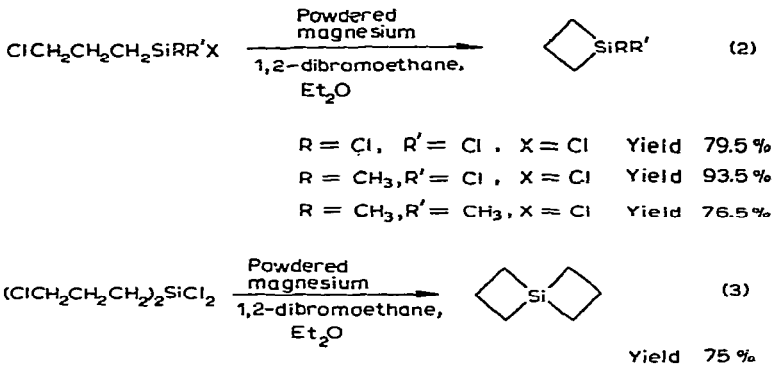
(1)

the active metal reagent. In general, 3-bromopropyl compounds can be cyclized in better yields than the 3-chloropropyl ones; however, the relatively high cost of allyl bromide, one of the reagents necessary to prepare the 3-bromopropyl derivatives, makes these less attractive cyclization precursors than the chloro compounds[1]. In most procedures using chloro precursors, prior activation of magnesium has been a necessary condition for high cyclization yields[1]. Among the activation procedures which have been employed are (1) increasing the surface area of the magnesium (either mechanically[2] or using powdered magnesium[3]), (2) chemical activation of the magnesium (iodine[4]), and (3) variation of solvent.

We have experienced difficulties with a variety of these procedures leading to either low (40–50%) or irreproducible yields. We, therefore, decided to investigate general (applicable to a variety of substitution patterns) activation procedures which would meet the criteria of high yield, reproducibility, and simplicity of activation.

We have found that the combination of increasing surface area and chemical activation has resulted in a highly efficient cyclization procedure for a variety of substituted (3-chloropropyl)chlorosilanes. Using chemical activation of powdered

magnesium by 1,2-dibromoethane we have carried out the following cyclizations in the yields indicated:



1,1- *Dichlorosilacyclobutane*

We had been able to prepare 1,1-dichloro-1-silacyclobutane in yields ranging from 25–84% by previously reported[1,3,4] procedures. Our best yields were obtained using (3-bromopropyl)trichlorosilane and ordinary magnesium turnings in ether. Nevertheless, this procedure proved delicate in that most runs under presumably identical conditions gave yields around 50%. With the 3-chloropropyl precursor we had similar difficulties with yields normally around 25%.

In marked contrast, activation of Baker powdered magnesium by 1,2-dibromoethane in ether gives the dichlorosilacyclobutane in 79.5% yield. The procedure is readily carried out with a simple workup.

1-*Chloro*-1-*methyl*-1-*silacyclobutane*

Preparation of this compound using literature procedures[1,3,4] gave yields ranging from 38–57%. The latter yield was accomplished with ordinary magnesium turnings in ether. Our activation procedure results in very high yields of the desired compound. The workup procedure must, however, include a slow, careful distillation through an efficient distillation column.

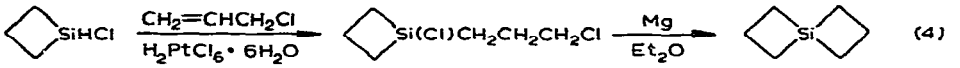
1,1-*Dimethyl*-1-*silacyclobutane*

We have had no recent occasion to prepare this compound by literature procedures. The best reported direct preparation[2]* involves activation of magnesium turnings by heating and stirring *in vacuo*[5] (61% yield). Our procedure is inferior to this although the GLC yield is 76.5%. Repeated attempts to isolate the product utilizing our other workup procedures have led to only very poor yields of 1,1-dimethylsilacyclobutane (up to 25%). We have been unable to develop a procedure for isolating high yields and there are indications that under the workup conditions polymerization occurs.

* 1,1-Dimethyl-1-silacyclobutane is prepared most readily by reaction of 1-chloro-1-methyl-1-silacyclobutane with a methyl Grignard. The more ready availability and cost of the precursors for this synthesis make it the most attractive one.

4-Silaspiro[3,3]heptane

The spiro compound has recently been reported by Nametkin and coworkers[6]. Two general methods of synthesis have been attempted [eqns. (4) and (5)].



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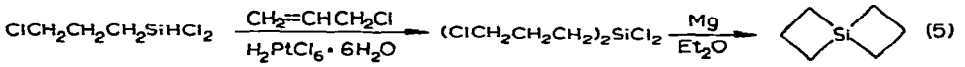
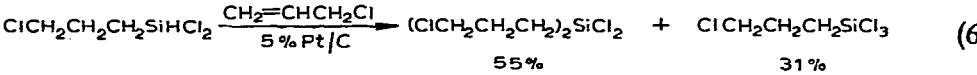


(5)

We have studied slightly different routes and report here variations of eqns. (4) and (5) which make the spiro compound more accessible. We find that hydrosilation of allyl bromide by 1-chloro-1-silacyclobutane gives an analogous adduct, 1-(3-bromopropyl)-1-chloro-1-silacyclobutane, in 19% yield. Our interest in this route faded when hydrosilation yields could not be improved; however, investigation of a path similar to eqn. (5) proved fruitful. Our initial attempts at hydrosilation with (3-chloropropyl)dichlorosilane using chloroplatinic acid were most frustrating. As indicated[6], this is a most delicate reaction; in our laboratories we never even approached the 56% yield which has since been reported[6]. We found, however, that 5% Pt on powdered charcoal gave reasonable and reproducible yields of adduct, eqn. (6). The reaction is carried out simply as the products are readily separable. None



(6)

of the difficulties indicated by Nametkin[6] and us using chloroplatinic acid catalysis has been encountered with platinum on charcoal. Finally, using our procedure for the activation of magnesium, we have been able to cyclize bis(3-chloropropyl)dichlorosilane to the spiro compound readily in 75% yields.

CONCLUSIONS

Because the previously reported methods for cyclization to silacyclobutanes have often proved difficult to reproduce, we have sought alternative cyclization methods. Activation of powdered magnesium with 1,2-dibromoethane in ether has been shown to give silacyclobutanes simply and efficiently. One drawback has been indicated in that 1,1-dimethyl-1-silacyclobutane is prepared in high yield (GLC) but cannot, under the conditions used, be isolated in yields greater than 25%.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen.

Gas–liquid partition chromatography (GLC) was used routinely for product detection. A Hewlett–Packard Model 700 (F and M) with linear temperature programer was used exclusively in this work. Infrared spectra were recorded using a Perkin–Elmer 237B grating infrared spectrophotometer; NMR spectra were recorded on a Varian Associates A-60A. Chemical shifts are expressed in δ units ppm downfield from tetramethylsilane. The mass spectra were recorded on an AEI MS-12 Mass Spectrometer.

Cyclization to the silacyclobutanes

The general cyclization procedure will be detailed for 1,1-dichloro-1-silacyclobutane. Only brief experimental details will be given for the other cyclizations detailing those operations which differ from the general procedure.

Preparation of 1,1-dichloro-1-silacyclobutane

A dry, 1-l, three-neck round-bottom flask equipped with a mechanical stirrer, dropping funnel, and condenser with nitrogen inlet system was charged with 18.3 g (0.75 mole) magnesium powder (J. T. Baker 2416) and 250 ml anhydrous diethyl ether. The magnesium was activated by the addition of 1 ml 1,2-dibromoethane and refluxing for 15 min. A solution of 53 g (0.25 mole) (3-chloropropyl)trichlorosilane[7] in 200 ml diethyl ether was added dropwise over a 3-h period at room temperature. The mixture was stirred for an additional 24 h. The magnesium chloride and excess magnesium were filtered under prepurified nitrogen. The residue was washed with two portions of ether. Slow distillation of the filtrate through a 30-cm Widmer column yielded a fraction (28.0 g, 79.5%) boiling at 55°/115 mm Hg, n_D^{25} 1.4464 [lit. b.p. 113–115°/760 mm Hg[3], n_D^{20} 1.4620[4]]. Its infrared spectrum (film) was in accord[3] with the structure having bands at 2980 m, 2940 s, 1380 s, 1120 vs, 990 m, 850 vs, 725 vs, and 690 vs cm^{-1}. NMR spectrum in CCl_4 showed a multiplet centered at δ 1.94. Characteristic mass spectra peaks occurred at 144(2), 142(10), 140(14), 127(8), 125(10), 116(12), 114(70), 112(10), 65(26), and 63(72).

Preparation of 1-chloro-1-methyl-1-silacyclobutane

Procedure 1. This was carried out with 0.25 mole of (3-chloropropyl)dichloromethylsilane[7]. After filtration and washings of the reaction mixture, the filtrate was slowly distilled through a 12 cm glass helix-packed column yielding a fraction (22.1 g, 73.4%) boiling at 91–3°/630 mm Hg, n_D^{25} 1.4477 [lit. b.p. 103.5–4°/731 mm Hg[4], n_D^{20} 1.4482[4]]. Infrared spectrum (film) 2970 s, 2920 s, 1380 m, 1250 s, 1120 s, 890 s, and 770 s cm^{-1}. NMR spectrum (CCl_4) δ 0.49 singlet (3H), δ 1.29 triplet (4H), and δ 1.90 multiplet (2H). Mass spectrum 122(8), 120(20), 105(8), 94(45), 92(100), 85(7), 79(18), 65(38), and 63(90).

Procedure 2. This was carried out with 0.50 mole of (3-chloropropyl)dichloromethylsilane. After reaction the volatiles were removed from the solid material by trap-to-trap distillation (10 mm Hg). Slow distillation of the distillate through a 12 cm glass helix-packed column yielded 56.4 g (93.5%) of 1-chloro-1-methyl-1-silacyclobutane.

Preparation of 1,1-dimethyl-1-silacyclobutane

This reaction was carried out with 73 mmole of (3-chloropropyl)dimethylchlorosilane. A number of attempts at workup by the above methods gave only poor yields.

Direct yield determinations by GLC (dibutyl ether as standard) showed the product to be formed in 76.5% yield, n_D^{25} 1.4247 (lit. n_D^{25} 1.4252[2]). Infrared spectrum (film) 2965 s, 2925 m, 2850 w, 1400 w, 1250 s, 1120 s, 885 s, 840 s, and 815 s cm^{-1}. NMR spectrum (CCl_4) δ 0.27 singlet (6H), δ 0.97 triplet (4H), and δ 2.05 multiplet (2H). Mass spectrum 101(3), 100(20), 85(8), 72(17), 73(100), 71(6), 70(9), 59(18), 58(5), and 57(5).

Preparation of 4-silaspiro[3,3]heptane

The synthesis was carried with 0.16 mole of bis(3-chloropropyl)dichlorosilane. After filtration and washings of the reaction mixture, the filtrate was distilled slowly through a 15 cm Vigreux column yielding a fraction (13.4 g, 75%) boiling at 45° /40 mm Hg, n_D^{25} 1.4852 [lit. b.p. 49°/mm Hg[6]]. Infrared spectrum (film) 2980 s, 2930 s, 2870 s, 1410 m, 1400 m, 1120 s, 952 s, 910 m, 840 s, and 710 s cm^{-1}. NMR (CCl_4) δ 1.19 triplet (8H) and δ 2.08 multiplet (4H). Mass spectrum 113(6.9), 112(48), 97(14), 85(14), 84(100), 83(56), 82(16), 70(8), 56(41), 55(18), 43(15), and 42(14).

Preparation of bis(3-chloropropyl)dichlorosilane

Into a dry 500-ml 1-necked flask equipped with reflux condenser, magnetic stirring bar, and N_2 inlet system were charged 130.2 g (0.73 mole) of (3-chloropropyl)-dichlorosilane[6], 64.0 g (0.74 mole) of allyl chloride, and 0.05 g of 5% platinum on charcoal (Matheson, Coleman, and Bell). The mixture was heated and stirred for 2 h at 80°. Distillation through a 30 cm Vigreux column yielded two main fractions, one boiling at 48–52°/4 mm Hg (48.6 g, 31%) identified as (3-chloropropyl)trichlorosilane and the other boiling at 121–5° /5 mm Hg [lit.[6] 100° /3 mm Hg] (102.7 g, 55%) identified as follows as bis(3-chloropropyl)dichlorosilane. Infrared spectrum (film) 2970 m, 2930 w, 2910 w, 1443 m, 1317 m, 1272 m, 1000–1170 s, 770 s, and 700 s cm^{-1}. NMR spectrum (CCl_4) δ 1.32 multiplet (2H), δ 2.04 multiplet (2H), and δ 3.67 multiplet (2H).

ACKNOWLEDGEMENTS

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