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TRIMETHYLHALOSILANE ELIMINATION FROM TRIMETHYLSILYL-SUBSTITUTED *gem*-DIHALOCYCLOPROPANES

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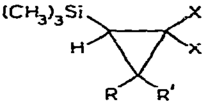
SUMMARY

The aluminum halide-catalyzed elimination of trimethylhalosilane from 1,1-dihalo-2-(trimethylsilyl)cyclopropanes (X = Cl and Br) resulted in the formation of propargyl halides, $HC{\equiv}CCH_2X$. Reaction of 1,1-dichloro-2,2-dimethyl-3-(trimethylsilyl)cyclopropane with sodium ethoxide in ethanol also resulted in elimination of trimethylchlorosilane; the organic product was 3-ethoxy-3-methyl-1-butyne, $HC{\equiv}C{-}CMe_2OEt$, and a mechanism involving β-elimination of trimethylchlorosilane to give 1-chloro-3,3-dimethylcyclopropene and reaction of the latter to produce the acetylenic ether is suggested.

INTRODUCTION

The β-elimination of silicon halide from 2-haloalkylsilanes was discovered by Sommer and Whitmore[1] when they found that (β-chloroethyl)trichlorosilane reacted smoothly with four equivalents of base to give silicate ion and ethylene. The study of such elimination reactions was extended by these workers to the elimination of trimethylchlorosilane from (β-chloroethyl)trimethylsilane in the presence of aluminum chloride or ethanolic base[2]. A later study by Sommer and Braugham[3] showed that the reaction with base involved a concerted, unimolecular elimination of trimethylchlorosilane from (β-chloroethyl)trimethylsilane.

The availability of *gem*-dihalocyclopropanes prepared by phenyl(bromodichloromethyl)mercury-derived dihalocarbene addition to vinylic silanes[4,5] suggested to us that a study of trimethylhalosilane elimination from compounds of type (I)



(I)

might be of some interest. In a concurrent investigation, the Lewis acid-catalyzed elimination of trimethylmetal halide from trimethylsilylmethyl- and trimethyltinmethyl-substituted *gem*-dihalocyclopropanes had been studied and information concerning the mechanism of such eliminations had been obtained[6].

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RESULTS AND DISCUSSION

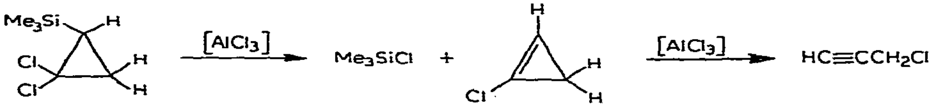
Since some compounds of type $R_3SiCH_2CH_2X$ are known to undergo β-elimination of R_3SiX simply on being heated, an attempt was made to decompose thermally 1,1-dibromo-2-(trimethylsilyl)cyclopropane, in the hope that trimethylbromosilane elimination might produce 1-bromocyclopropene. However, this silane survived distillation at atmospheric pressure (b.p. 190–191°). In view of the fact that Lewis acids promote such β-elimination reactions, the decomposition of 1,1-dichloro-2-(trimethylsilyl)cyclopropane in the presence of aluminum chloride was studied*. When this cyclopropane was added dropwise to a slurry of aluminum chloride (*ca.* 20 mole %, based on the cyclopropane) in carbon tetrachloride (under nitrogen), an exothermic reaction occurred, which could be controlled by suitable adjustment of the rate of addition. The products formed in this reaction were found to be trimethylchlorosilane and 3-chloro-1-propyne (propargyl chloride), in 3 : 1 ratio [eqn. (1)].

(1)

The organic product yield was low (~20%) and the larger amount of the trimethylchlorosilane suggested that much of the cyclopropyl fragment formed in the elimination did not survive the reaction conditions. An attempt to promote this elimination with zinc chloride, a milder Lewis acid, failed; the cyclopropane was recovered unchanged.

Similar treatment of 1,1-dibromo-2-(trimethylsilyl)cyclopropane with aluminum bromide gave trimethylbromosilane and propargyl bromide (in *ca.* 30% yield). The presence of a small amount of the isomeric bromoallene was indicated by bands characteristic of the allene structure in the IR spectrum of the isolated propargyl bromide.

Further information was sought concerning these elimination reactions by a study of the aluminum chloride-catalyzed decomposition of *cis*- and *trans*-1,1-dichloro-2-methyl-3-(trimethylsilyl)cyclopropanes. However, in both cases the only volatile products were trimethylchlorosilane and a small amount of dimethyldichlorosilane. The organic products of these reactions appeared not to have survived the reaction conditions. In the absence of further information, one can only suggest possible courses of these elimination reactions: (*a*) one in which the formation of propargyl halide proceeds via an intermediate cyclopropene [eqn. (2)], and (*b*) one in which an allylic cation is formed, with or without the intermediate formation of 2,3-dichloro-1-(trimethylsilyl)propene [eqn. (3)]. In the case of the trimethylmetal halide elimination from trimethylmetalmethyl-substituted *gem*-dihalocyclopropanes a mechanism involving disrotatory, stereospecific opening of the cyclopropane ring to an allylic cation from which the trimethylmetal moiety is lost to give a 1,3-diene was discussed[6].



(2)

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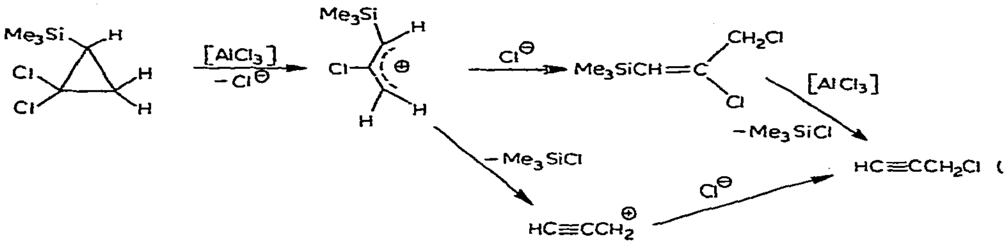
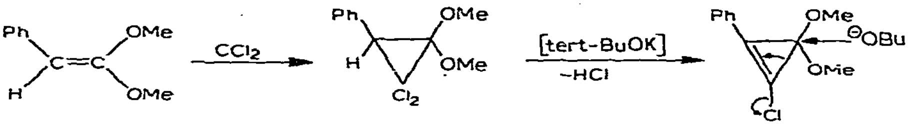
* Under conditions of Lewis acid catalysis, the sought-after halocyclopropenes would not be expected, since cyclopropenes are known to undergo facile, acid-catalyzed rearrangements[7].



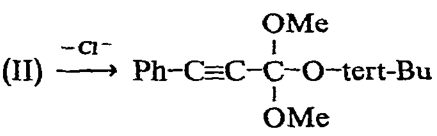
(3)

The possibility of β-elimination of trimethylchlorosilane from trimethylsilyl-substituted *gem*-dichlorocyclopropanes under basic conditions also was investigated briefly. In an initial experiment, 1,1-dichloro-2,2-dimethyl-3-(trimethylsilyl)cyclopropane was heated to reflux with an excess of potassium hydroxide in absolute ethanol for 2.5 h. A crystalline solid formed which dissolved when the reaction mixture was hydrolyzed, and analysis of the organic products showed that hexamethyldisiloxane (*ca.* 40%) and 3-ethoxy-3-methyl-1-butyne (*ca.* 20%) had been obtained, as well as a small amount of another product (*ca.* 2%), which was identified by means of its infrared spectrum as the allene isomeric with the acetylenic ether. When 1,1-dichloro-2,2-dimethyl-3-(trimethylsilyl)cyclopropane was treated with an excess of sodium ethoxide in refluxing absolute ethanol in a similar experiment, 3-ethoxy-3-methyl-1-butyne again was obtained (26%), along with 2–3% of the allenic isomer.

Some work of McElvain and Weyna[8] is pertinent in this connection. In their attempted preparation of 1,1-dichloro-2,2-dimethoxy-3-phenylcyclopropane by the addition of dichlorocarbene (generated via $CHCl_3$ + tert-BuOK) to 1,1-dimethoxy-2-phenylethylene, the final product obtained was 3,3-dimethoxy-3-tert-butoxy-1-phenyl-1-propyne. The formation of this product was explained in terms of the process shown in the sequence below:

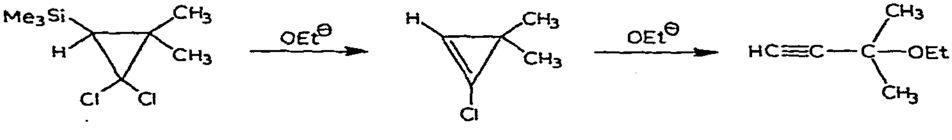


(II)



$$(II) \xrightarrow{-Cl^-} Ph{-}C{\equiv}C{-}\underset{OMe}{\overset{OMe}{C}}{-}O{-}tert{-}Bu$$

A similar reaction of the 1-chlorocyclopropene obtained by the β-elimination of trimethylchlorosilane from 1,1-dichloro-2,2-dimethyl-3-(trimethylsilyl)cyclopropane could account for the formation of the acetylenic ether:



Further reinforcing these arguments is the fact that Gardner and coworkers[9] have been able to prepare 1-chloro-3,3-dimethyl-2-tert-butylcyclopropene by the reaction of 1,1-dichloro-2,2-dimethyl-3-tert-butylcyclopropane with potassium tert-butoxide in dimethyl sulfoxide.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen unless otherwise noted. The preparation of the starting silylcyclopropanes has been described in previous papers from this Laboratory[4,5]. The aluminum halides were reagent grade and were used without further purification. The product mixtures were analyzed by gas-liquid partition chromatography (GLPC) using an MIT isothermal unit. Samples of the products were collected by trapping eluted components in U-shaped 6 mm glass tubes equipped with a no-air stopper and a short, Drierite-filled tube. The sample collectors were swept with nitrogen immediately before use and samples were handled in glass syringes under nitrogen. Yields were determined by GLPC. IR spectra were determined using a Perkin–Elmer Model 237 or 337 grating IR spectrophotometer, generally in carbon tetrachloride solution. NMR spectra were determined with a Varian Associates A60 NMR spectrometer. Chemical shifts are given in ppm downfield from internal tetramethylsilane.

Decomposition of 1,1-*dichloro*-2-(*trimethylsilyl*)*cyclopropane in the presence of aluminum chloride*

Into a dry, 50 ml, three-necked flask equipped with a 60 ml dropping funnel, a water-cooled reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was charged 0.67 g (5.0 mmoles) of aluminum chloride and 10 ml of dry carbon tetrachloride under a nitrogen atmosphere. The mixture was stirred while a solution of the cyclopropane (4.19 g, 22.9 mmoles) in 5 ml of carbon tetrachloride was added dropwise over a 30 min period*. A purple color developed in the reaction mixture immediately and became more intense as the addition proceeded. Sufficient heat was evolved to cause the reaction solution to reflux. After the addition was completed, the dropping funnel and condenser were removed under a positive pressure of nitrogen, and the flask was connected to a receiving flask via a curved glass tube. The volatiles were transferred into the receiver (cooled to −78°) in a simple trap-to-trap distillation at 10 mm (pot temperature to 25°). A clear distillate which fumed on exposure to air was obtained. The distillate was analyzed by GLPC (25% Dow Corning 710 Fluid on Chromosorb P, 72°, 15 psi helium), and only two components in a ratio of about 3:1 were observed, in addition to the solvent. The first component to be eluted was identified as trimethylchlorosilane (IR spectrum and GLPC retention time), the second as propargyl chloride by comparison of its IR spectrum with that published for this acetylene[10]. The yields of these products were 58% and 22%, respectively. The NMR spectrum (in CCl_4) of the propargyl chloride produced showed a doublet at 4.07 ppm ($J=2.5$ cps; 2H) and a triplet at

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* Addition in the inverse manner—that is, of aluminum chloride to the dihalocyclopropylsilane—resulted in a violent reaction which gave a dark, tarry residue and a dense, purple vapor.

2.40 ppm ($J=2.5$ cps; 1H), in agreement with that reported for propargyl chloride[11].

In a separate experiment 1,1-dichloro-2-(trimethylsilyl)cyclopropane (30.6 mmoles) was heated (oil bath at 130°) with anhydrous zinc chloride (3.8 mmoles) for 6 h under (nitrogen) atmospheric pressure, but the cyclopropane was recovered without change.

Decomposition of 1,1-*dibromo-2-(trimethylsilyl)cyclopropane in the presence of aluminum bromide*

The cyclopropane (5.16 g, 18.9 mmoles) was added to anhydrous aluminum bromide (0.296 g, 1.1 mmoles) in 10 ml of methylene chloride, following the procedure described in the previous experiment. The initially clear mixture became purple-black as the addition progressed. After all of the cyclopropane had been added, the volatiles were trap-to-trap distilled away from a black, viscous residue at 25° and 60 mm. The clear distillate was analyzed by GLPC (710 Fluid, 80°, 12 psi helium). Two components were eluted after the solvent peak in an area ratio of about 3:2, with retention times of 13.8 min (small shoulder at about 15 min) and 16.0 min, respectively. The latter product was identified as propargyl bromide by comparison of its IR spectrum with that reported for this compound[10]. Impurity bands at 3090, 1955 and 1042 cm^{-1} were attributable to bromoallene[10]. The NMR spectrum of the propargyl bromide showed a doublet at 3.96 ppm ($J=2.5$ cps; 2H) and a triplet at 2.46 ppm ($J=2.5$ cps; 1H). Its yield was 30%, based on the starting cyclopropane.

The component with shorter retention time was identified as trimethylbromosilane by means of its GLPC retention time and by hydrolyzing it to hexamethyldisiloxane. The latter was identified by means of its GLPC retention time and its IR spectrum. The yield of trimethylbromosilane was 47%, as determined by GLPC analysis (external standard method) of the initial distillate.

Reaction of 1,1-*dichloro-2,2-dimethyl-3-(trimethylsilyl)cyclopropane with potassium hydroxide in ethanol*

Potassium hydroxide pellets (2.89 g, 62.6 mmoles) were dissolved in 25 ml of absolute ethanol in a 50 ml, three-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. The resulting solution was heated to reflux (under nitrogen) and the cyclopropane (7.28 g, 10.3 mmoles) was added dropwise with stirring. The solution gradually developed an orange color and a crystalline solid precipitated. The mixture was heated at reflux for 2.5 h, cooled and poured into a separatory funnel containing 50 ml of water. The crystalline solid dissolved in the aqueous medium, but a small amount of insoluble orange residue remained. The aqueous layer was extracted with pentane and subsequently the dried pentane extracts were distilled to remove solvent. About 4 ml of dark yellow liquid remained which was analyzed by GLPC (710 Fluid, 98°, 20 psi helium). Two components were eluted after the solvent peak in about 2:1 ratio, with retention times of 6.2 min (shoulder at 5.8 min) and 10.3 min. The first component was identified as hexamethyldisiloxane, the second as 3-ethoxy-3-methyl-1-butyne on the basis of its NMR and IR spectra. The IR spectrum contained bands characteristic of tert-acetylenic ethers[12] at 3310 s, 2940 m, 1445 m, 1360 m and 1078 s cm^{-1}. The NMR spectrum (in CCl_4) showed a triplet at 1.09 ppm ($J=7$ cps; 3H), a sharp singlet at 1.35 ppm (6H), a singlet at 2.21 ppm (1H) and a quartet at 3.48 ppm ($J=7$ cps; 2H). The n_D^{25} of 1.3999 agreed well with that reported for this compound in the literature n_D^{25} 1.4002[12]. The yield of 3-ethoxy-3-methyl-1-butyne was about 20%.

The original mixture also was analyzed using a 9 ft × 10 mm column packed with 15% General Electric Co. XF-1150 on Chromosorb P at 79° and 15 psi helium. Under these conditions hexamethyldisiloxane was eluted in 2.0 min, the acetylenic ether in 4.2 min, and a third component in *ca.* 10% the amount of the acetylenic ether appeared at 8.7 min. The latter was collected; its IR spectrum (CCl_4) showed absorptions at 3030 (sh), 2980 s, 2960 (sh), 2935 s, 2910 (sh), 2875 (sh), 2725 w, 1955 s, 1720 m, 1685 s, 1455 s, 1445 (sh), 1400 m, 1385 m, 1375 m, 1360 m, 1280 m, 1260 m, 1223 w, 1200 w, 1178 w, 1125 s, 1070 m, 1044 (sh), 1030 (sh), 1008 (sh), 995 (sh), 970 w, 855 m and 850 (sh) cm^{-1}. The absorptions at 3030 (H–C=C=C), 1955 (C=C=C) and 1125 (C–O) cm^{-1} suggests that this compound is an allenic isomer of 3-ethoxy-3-methyl-1-butyne[13].

Reaction of 1,1-*dichloro*-2,2-*dimethyl*-3-(*trimethylsilyl*)*cyclopropane with sodium ethoxide in ethanol*

In a similar reaction 11.1 mmoles of the cyclopropane was added to sodium ethoxide prepared from 1.20 g (52 mg-atom) of sodium in 25 ml of absolute ethanol. The reaction mixture was heated at reflux for 24 h. The dark orange mixture was poured into 50 ml of water and extracted with pentane. The liquid residue upon evaporation of the pentane was analyzed by GLPC (82°, 15 psi helium). Hexamethyldisiloxane was present and 3-ethoxy-3-methyl-1-butyne had been formed in 26% yield. Use of the XF-1150 column again showed the presence of a minor amount of allenic impurity.

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REFERENCES

1 L. H. Sommer and F. C. Whitmore, *J. Amer. Chem. Soc.*, 68 (1946) 485.
2 L. H. Sommer, D. L. Bailey and F. C. Whitmore, *J. Amer. Chem. Soc.*, 70 (1949) 2869.
3 L. H. Sommer and G. A. Braugham, *J. Amer. Chem. Soc.*, 83 (1961) 3346.
4 D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber and S. R. Dowd, *J. Amer. Chem. Soc.*, 87 (1965) 4259.
5 D. Seyferth, T. F. Jula, H. Dertouzos and M. Pereyre, *J. Organometal. Chem.*, 11 (1968) 63.
6 D. Seyferth and T. F. Jula, *J. Amer. Chem. Soc.*, 90 (1968) 2938.
7 G. L. Closs, *Advan. Alicyclic Chem.*, 1 (1966) 91.
8 S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.*, 81 (1959) 2579.
9 T. C. Shield, B. A. Loving and P. D. Gardner, *Chem. Commun.*, (1967) 556.
10 J. C. Evans and R. A. Nyquist, *Spectrochim. Acta*, 19 (1963) 1156.
11 G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, 39 (1963) 3510.
12 G. F. Hennion and A. P. Bisselle, *J. Org. Chem.*, 26 (1961) 2677.
13 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, 2nd ed., 1958, pp. 58, 115.