Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

ORGANOSILICON COMPOUNDS
XL*. RATES OF RING-OPENING OF SOME BENZOSILACYCLOALKENES

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(Received February 1st, 1967)

INTRODUCTION

Four-membered rings containing silicon and carbon atoms are known to undergo ring-opening very readily by cleavage of Si–C bonds[2,3], whereas five- and six-membered rings are opened with much greater difficulty[3]. To provide quantitative measures of the ease of such ring-opening, we have examined the effect of acid and alkali on 1,1-dimethyl-2,3-benzo-1-sila-2-cyclo-butene, (I), -pentene, (II), and -hexene, (III), and for comparison, on some corresponding compounds in which the silicon atom is not in a ring system.

RESULTS AND DISCUSSION

Various routes to 2,3-benzo-1-silacycloalkenes are available[4,5,6], and we have used established cyclization procedures without significant modification to prepare compounds (I), (II), and (III). The assigned structures are in agreement with the nature of the products from ring-opening, and the NMR spectra are as expected by comparison with those of 1,1-diphenyl-2,3-benzo-1-sila-2-cycloalkenes[4,5].

Acid cleavage

The rates of cleavage of the aryl–silicon bonds in compounds (I)-(III) by aqueous methanolic perchloric acid were measured spectrophotometrically (*cf.* ref. 7). The results are given in Table 1, which lists the values of k_1, the observed first-order rate constants, of k_{rel}, the rates relative to that for phenyltrimethylsilane at 50°, and approximate values of the energy of activation, E_{Act}. Corresponding figures for some related compounds are also listed.

It will be seen that the aryl–silicon bond in the cyclobutene derivative, (I), is cleaved by acid some 440 times as readily as that in the compound o-$CH_3C_6H_4SiMe_3$ and 240 times as readily as that in the more closely analogous compound o-$Me_3SiCH_2C_6H_4SiMe_3$[8]. These are not very large factors, and the enhancement of the reactivity of the cyclic compounds can be explained in terms of a release of angle strain as a proton attaches to the ring carbon atom to form the Wheland intermediate (IV), with change in the configuration of this carbon atom from trigonal to tetrahedral. This would be consistent with operation of the mechanism proposed for the cleavage

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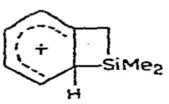
* For part XXXIX see ref. 1.

TABLE 1

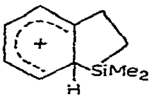
THE CLEAVAGE OF $XC_6H_4SiMe_3$ COMPOUNDS AND OF BENZOSILACYCLOALKENES AT 35.0° AND 50.0°

Compound	*[$HClO_4$]*[a] *(M)*	10^3k_1(35°) *(min^{-1})*	10^3k_1(50°) *(min^{-1})*	k_{rel}[b]	λ[c]	E_{Act} *(kcal/mole)*
(a) Medium: Methanol (5 vol) plus aqueous perchloric acid (2 vol)						
o-$MeC_6H_4SiMe_3$	12.4	20.2	97.6	17.8[d]	272	20.1
	9.4		26.1			
o-$Me_3SiCH_2C_6H_4SiMe_3$				31[e]		
o-$EtC_6H_4SiMe_3$	12.4	18.1	90.1	16.4	272	20.6
o-$Me_3SiCH_2CH_2C_6H_4SiMe_3$				17[e]		
o-$PrC_6H_4SiMe_3$	12.4		85.0	15.5	272	
o-$Me_3Si(CH_2)_3C_6H_4SiMe_3$				12[e]		
p-$MeOC_6H_4SiMe_3$	2.0		29.3	1510[d]	282	
(III)	9.4	26.3	127	86.6	275.5	20.1
(II)	12.4	15.4	82.1	15.0	275.5	21.5
(I)	2.0	53.1	191	9840	276	16.2
(b) Medium: A, methanol; B, methanol (10 vol) plus water (2 vol)						
(I) (medium A)		39.4	139		276	16.0
(I) (medium B)		62.2	262		276	18.3

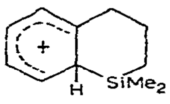
[a] Concn. of the aqueous perchloric acid. [b] Rate relative to trimethylphenylsilane at 50°. [c] Wavelength at which the absorption was recorded. [d] Value from ref. 7. [e] Value from ref. 8.



(IV)



(V)



(VI)

of aryltrialkylsilanes in which proton attachment is rate-determining and fission of the aryl–silicon bond occurs in a fast subsequent step[9]. It is possible that strain in (I) causes ring-opening to occur synchronously with protonation at carbon, with avoidance of the intermediate (IV), but the rate enhancement is not large enough to require such a mechanistic change.

The rate of ring-opening of the cyclopentene derivative, (II), is not significantly different from that expected by comparison with the corresponding o-Me_3SiCH_2-$CH_2C_6H_4SiMe_3$[8] or o-$CH_3CH_2C_6H_4SiMe_3$ compounds. The rate for the cyclohexene derivative (III), however, is some five to seven times as great as that for its non-cyclic analogues and, probably more significantly, is about six times as great as that for compound (II). This factor seems too great to be accounted for by any difference in electronic effects in the two system, and it seems that there must be small but significant steric strain in compounds (II) and (III) which is relieved to some extent by protonation in the case of (III), to give (VI), but not, or not as much, in the case of (II), to give (V). This would be in accord with the generalization by Brown and his co-workers that strain (which in these cases is attributable primarily to repulsion terms arising from unfavourable conformations rather than to bond angle deformation[10]) is increased when a tetrahedral replaces a trigonal atom in a 5-membered ring carbon but is decreased when such a replacement is made in a six-membered ring[11].

Alkali cleavage

As was expected by analogy with the behaviour of $ArSiMe_3$ and $Ar(CH_2)_nSiMe_3$ ($n > 1$) compounds, no ring-opening of compounds (II) and (III) took place in aqueous methanolic alkali of the strength used to cleave the compound $PhCH_2SiMe_3$[12]. In contrast, the silacyclobutene (I) was found to be cleaved quite rapidly by methanol alone, and examination of the products showed that fission of the $Ar-CH_2SiMe_2$ bond had occurred exclusively, to give the methoxide o-$MeC_6H_4SiMe_2OMe$. The rate was increased by the addition of water, and very greatly by a trace of alkali, and was completely inhibited by a trace of acid. (Cleavage of the aryl–silicon bond occurs, of course, if the acid concentration is increased, as described above.) This indicates that methoxide-ion produced by autoprotolysis is responsible for the neutral cleavage, not methanol itself. By comparison with the rate of cleavage in aqueous methanol of (p-nitrobenzyl)trimethylsilane, which itself is cleaved 1.8×10^6 times as fast as benzyltrimethylsilane[12], it can be concluded that the benzyl–silicon bond in compound (I) is broken at least 10^{10} times as readily as that in benzyltrimethylsilane.

It is known that in the cleavage of benzyltrimethylsilanes and related compounds the rate-determining step is either the synchronous attack of hydroxide (or alkoxide) ion on silicon and fission of the R_3Si-CH_2Ar bond, or the fission of this bond in the intermediate $[ArCH_2SiR_3OH]^-$ [12]. In either case the transition state of the rate-determing step would have some of the character of an sp^3d pentacoordinate-silicon intermediate[13] in which a 90° angle would be available for the $Ar-SiMe_2-CH_2$ angle. Thus strain would be rather less than in the starting compound (I), and would be further considerably relieved by stretching of the $ArCH_2-Si$ bond undergoing fission. The big difference with compound (I) between the enhancement relative to the acyclic analogues for acid cleavage of the Ar–Si bond and that for alkali-cleavage of the $ArCH_2-Si$ bond is consistent with our view that the ring is opened in the rate-determining step in the latter but not in the former reaction.

EXPERIMENTAL

Preparation of (o-methyl-, o-ethyl-, and o-propylphenyl)trimethylsilane

A mixture of o-chlorotoluene (25.2 g, 0.20 mole) and chlorotrimethylsilane (23.7 g, 0.22 mole) was added carefully to molten sodium (9.7 g, 0.42 g-atom) dispersed in refluxing toluene (80 ml). The mixture was subsequently refluxed for 0.5 h, cooled, and filtered. Precipitated material was washed with warm toluene (50 ml) and the combined filtrates were distilled to give (o-methylphenyl)trimethylsilane (80%), b.p. 196°, n_D^{25} 1.5005 (lit.[14] b.p. 196°).

Similarly, from the corresponding o-alkylchlorobenzenes, were prepared (o-ethylphenyl)trimethylsilane (70%), b.p. 82°/8.5 mm, n_D^{25} 1.5018, (Found: C, 74.1; H, 10.1. $C_{11}H_{18}Si$ calcd.: C, 74.1; H, 10.2%.) and (o-propylphenyl)trimethylsilane (72%), b.p. 75°/2.5 mm, n_D^{25} 1.5020. (Found: C, 74.7; H, 10.5. $C_{12}H_{20}Si$ calcd.: C, 74.9; H, 10.5%.)

1,1-Dimethyl-2,3-benzo-1-sila-2-cyclobutene (I).

A mixture of *o*-bromobenzyl bromide (66 g, 0.26 mole) and dichlorodimethylsilane (36.4 g, 0.28 mole) in ether (265 ml) was added to magnesium turnings (19. 4 g, 0.8 g-atom) in refluxing ether (55 ml) during 6 h. The reaction mixture was cooled and treated with saturated ammonium chloride. The ethereal layer was separated, dried, and fractionated to give 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene (35%), b.p. 73°/17 mm, n_D^{25} 1.5228. (Found C, 72.7; H, 8.1. $C_9H_{12}Si$ calcd.: C, 72.9; H, 8.2%.)

1,1-Dimethyl-2,3-benzo-1-sila-2-cyclopentene (II)

A filtered solution of the di(bromomagnesium) reagent prepared from 2-(*o*-bromophenyl)ethyl bromide[6] (64 g, 0.24 mole) and magnesium (19.4 g, 0.80 g-atom) in tetrahydrofuran (500 ml) was added to dichlorodimethylsilane (26 g, 0.20 mole) in the same ether (100 ml). The reaction mixture was refluxed for 1 h, and treated with aqueous ammonium chloride, and the usual working-up gave 1,1-dimethyl-2,3-benzo-1-sila-2-cyclopentene (15%), b.p. 83°/15 mm, n_D^{25} 1.5202. (Found: C, 73.9. H, 8.5. $C_{10}H_{14}Si$ calcd.: C, 74.0; H, 8.7%.)

[3-(o-Chlorophenyl)propyl] dimethylsilane

The Grignard reagent prepared from 3-(*o*-chlorophenyl)propyl bromide[5] (107 g, 0.46 mole) and magnesium (15.6 g, 0.64 g-atom) in ether (600 ml) was filtered and added at 0° to chlorodimethylsilane (40 g, 0.42 mole) in ether (40 ml). The mixture was refluxed for 6 h, then worked up in the usual way to give [3-(*o*-chlorophenyl)-propyl]dimethylsilane (80%), b.p. 50°/0.1 mm, n_D^{25} 1.5160. (Found: C, 61.9; H, 8.0; Cl, 16.7. $C_{11}H_{17}ClSi$ calcd.: C, 62.1; H, 8.1; Cl, 16.7%.)

Chloro[3-(o-chlorophenyl)propyl] dimethylsilane

To [3-(*o*-chlorophenyl)propyl]dimethylsilane (74 g, 0.35 mole) in carbon tetrachloride (80 ml) N-chlorosuccinimide (46.5 g, 0.35 mole) was added at 0–10° during 1 h. After a further 1 h of refluxing, precipitated succinimide was filtered off and washed with carbon tetrachloride (150 ml), and the combined filtrates were fractionated to give chloro-[3-(*o*-chlorophenyl)propyl]dimethylsilane (85%), b.p. 67°/0.1 mm. (Found: C, 53.6; H, 6.5; Cl, 28.6. $C_{11}H_{16}Cl_2Si$ calcd.: C, 53.4; H, 6.5; Cl, 28.7%.)

1,1-Dimethyl-2,3-benzo-1-sila-2-cyclohexene (III)

Chloro[3-(*o*-chlorophenyl)propyl]dimethylsilane (35 g, 0.14 mole) in toluene (100 ml) was added to molten sodium (6.7 g, 0.29 mole) in refluxing toluene (100 ml) during 1 h. The reaction mixture was refluxed for a further 2 h, then cooled and filtered, and the filtrate was distilled to give 1,1-dimethyl-2,3-benzo-1-sila-2-cyclohexene (35%), b.p. 53°/0.5 mm, n_D^{25} 1.5248. (Found: C, 75.0; H, 9.1. $C_{11}H_{16}Si$ calcd.: C, 74.9; H, 9.2%.)

Chlorodimethyl-o-tolylsilane

The organolithium reagent prepared from *o*-bromotoluene (68 g, 0.4 mole) and lithium shot (6.9 g, 1.0 g-atom) in ether (350 ml) was added at 0° during 2 h to dichlorodimethylsilane (117 g, 0.9 mole) in ether (60 ml). The mixture was refluxed for 1 h, the precipitated salts were filtered off, and the filtrate was fractionated to give chlorodimethyl-*o*-tolylsilane (72%), b.p. 210°, n_D^{25} 1.5210. (Found: C, 58.4; H, 7.1; Cl, 19.1. $C_9H_{13}ClSi$ calcd.: C, 58.5; H, 7.1; Cl, 19.2%.)

Dimethylmethoxy-o-tolylsilane

Chlorodimethyl-*o*-tolylsilane (20 g, 0.11 mole) was added to a mixture of anhydrous methanol (6 g), triethylamine (12.1 g), and ether (100 ml). The mixture was refluxed for 1 h, precipitated salts were filtered off, and the filtrate was concentrated and distilled to give dimethylmethoxy-*o*-tolylsilane (90%), b.p. 84°/8.5 mm, n_D^{25} 1.4948. (Found: C, 66.5; H, 8.8. $C_{10}H_{16}OSi$ calcd.: C, 66.6; H, 9.0%.)

Chlorodimethyl(2-phenylethyl)silane

The Grignard reagent prepared from 2-phenylethyl bromide (60 g, 0.30 mole) and magnesium (9.7, 0.40 g-atom) in ether (300 ml) was filtered and added during 3 h at 0° to dichlorodimethylsilane (78 g, 0.60 mole) in ether (80 ml). The mixture was set aside for 24 h, precipitated magnesium salts were filtered off, and the filtrate was evaporated. After removal of *ca.* 300 ml of ether the reaction mixture was refiltered, and the filtrate was distilled to give chlorodimethyl(2-phenylethyl)silane (67%), b.p. 56°/0.2 mm. (Found: C, 60.3; H, 7.6; Cl, 17.6. $C_{10}H_{15}ClSi$ calcd.: C, 60.4; H, 7.6; Cl, 17.8%.)

Chlorodimethyl(3-phenylpropyl)silane

A similar procedure involving 3-phenylpropylmagnesium bromide and dichlorodimethylsilane gave chlorodimethyl(3-phenylpropyl)silane (60%), b.p. 75°/0.5 mm. (Found: C, 62.2; H, 8.0; Cl, 16.7. $C_{11}H_{17}ClSi$ calcd.: C, 62.1; H, 8.1; Cl, 16.7%.)

1,3-*Bis*(2-*phenylethyl*)-1,1,3,3-*tetramethyldisiloxane*

A mixture of chlorodimethyl-(2-phenylethyl)silane (30 g), dioxane (120 ml), water (30 ml) and concentrated hydrochloric acid (5 ml) was boiled for 0.5 h. Hydrolysis, ether extraction and working up gave 1,3-bis(2-phenylethyl)-1,1,3,3-tetramethyldisiloxane (90%), b.p. 135°/0.1 mm, n_D^{25} 1.5018. (Found: C, 70.0; H, 8.8. $C_{20}H_{30}OSi_2$ calcd.: C, 70.1; H, 8.8%.)

1,3-*Bis*(3-*phenylpropyl*)-1,1,3,3-*tetramethyldisiloxane*

Chlorodimethyl(3-phenylpropyl)silane was hydrolysed in a similar manner to give 1,3-bis(3-phenylpropyl)-1,1,3,3-tetramethyldisiloxane (86%), b.p. 140°/0.1 mm, n_D^{25} 1.5013. (Found: C, 71.2; H, 9.3. $C_{22}H_{34}OSi_2$ calcd.: C, 71.3; H, 9.3%.)

Rate studies

The acid cleavage of aryl–silicon bonds in the compounds $XC_6H_4SiMe_3$ and in the 1,1-dimethyl-2,3-benzo-1-sila-2-cycloalkenes, and the neutral methanolysis of 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene were followed spectrophotometrically at 35.0 and 50.0°, at the wavelengths given in Table 1, by the method previously described[7]. For acid cleavages, rate measurements were conducted in a mixture of aqueous perchloric acid (2 vol) with a methanolic solution (5 vol) of the organosilicon compound. Slightly acidified methanol was used for preparing stock solutions of (*p*-methoxyphenyl)trimethylsilane and of 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene in order to prevent any cleavage of the benzylsilicon bond in the latter before mixing with aqueous acid.

Freshly distilled methanol and boiled-out water were used for the neutral solvolysis of 1,1-dimethyl-2,3-benzo-1-sila-2-cyclobutene.

Cleavage products

(*i*) *Methanolysis of* 1,1-*dimethyl*-2,3-*benzo*-1-*sila*-2-*cyclobutene*. The organosilane (8.0 g, 0.05 mole) and methanol (200 ml) were refluxed for 1 h. Distillation gave pure dimethylmethoxy-*o*-tolylsilane (8.5 g, 92%) b.p. 71°/4 mm, and no by-products were detected.

(*ii*) *Acid cleavage of compounds* (*I*), (*II*), *and* (*III*). Compound (I) (9.6 g, 0.06 mole) was added to a mixture of methanol (200 ml) and 6 *M* aqueous perchloric acid (20 ml). The mixture was refluxed for 4 h then added to saturated aqueous ammonium chloride. Organic products were extracted with ether and the extract was dried and distilled to give 1,3-dibenzyl-1,1,3,3-tetramethyldisiloxane (82%), b.p. 136°/0.3 mm, n_D^{25} 1,5170. (lit.[15] b.p. 127°/0.15 mm, n_D^{25} 1.5157).

Similar treatment of compound (II) gave 1,3-bis(2-phenylethyl)-1,1,3,3,-tetramethyldisiloxane (78%), b.p. 145°/0.2 mm. Compound (III) likewise gave 1,3-bis-(3-phenylpropyl)-1,1,3,3-tetramethyldisiloxane (74%), b.p. 150°/0.2 mm.

NMR studies

NMR spectra were recorded on a Perkin Elmer Model R10 Spectrometer operating at 60 Mc. with tetramethylsilane as internal standard. Table 2 lists τ-values for the sila-2-cycloalkene ring protons, numbered according to the recommended scheme[5], of compounds (I), (II), and (III), and corresponding figures for 1,1-diphenyl-2,3-benzo-1-sila-2-cycloalkenes[4,5]. Integrated spectra of (I), (II), and (III) agreed with the assigned structures.

TABLE 2

NMR SPECTRA OF 1,1-DIPHENYL- AND 1,1-DIMETHYL-2,3-BENZO-1-SILA-2-CYCLOALKENES

Compound	*τ Values*		
	H(*C*-4)	*H*(*C*-5)	*H*(*C*-6)
1,1-Diphenyl-2,3-benzo-1-sila-2-cyclobutene[a]	7.54[c]		
(I)[b]	7.88[c]		
1,1-Diphenyl-2,3-benzo-1-sila-2-cyclopentene[a]	6.85[d]	8.57[d]	
(II)[b]	7.00[d]	9.12[d]	
1,1-Diphenyl-2,3-benzo-1-sila-2-cyclohexene[a]	7.13[d]	7.97[c]	8.63[e]
(III)[b]	7.33[d]	8.16[e]	9.19[d]

[a] Solution inCCl_4 (*cf.* ref. 4, 5). [b] Neat liquid. [c] Singlet. [d] Triplet. [e] Multiplet.

ACKNOWLEDGEMENTS

We thank Mr. M. R. JENSEN for determining the NMR spectra, the Royal Society for the loan of apparatus, and Midland Silicones Ltd., for a gift of chemicals.

SUMMARY

1,1-Dimethyl-2,3-benzo-1-sila-2-cyclo-butene, (I), -pentene, (II), and -hexene, (III), have been prepared, and quantitative measures obtained of the ease of ring-opening (*i*) by acid, with cleavage of the Ar–Si bond, of all three compounds, and (*ii*) by alkali, with cleavage of the $ArCH_2$–$SiMe_2$ bond, of compound (I). The results are discussed in terms of relief of strain in some of the reactions.

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