

Figure 1.—CO₂ evolution at 80° in benzene from mixed salts of LTA and dicarboxylic acids.

position,⁸ whereas methylene insertion produces only 2-picoline.⁹ This in fact offers a convenient test for the nature of an attacking reagent, when suitable, since analysis can easily be made by vpc. Methylene diacetate is also produced, in less than 1% yield. This could have resulted from the malonic acid,¹⁰ but has been found in decompositions of LTA alone.⁶ One other unidentified product was detected in trace amounts; it is probably an α -acetoxypicoline.¹¹ Polymeric materials similar to those obtained by Bartlett and Gortler from peroxy derivatives of malonic acid¹² could not be detected.

Contrary to Kochi's results with pentanoic acids,¹³ the rate of total gas evolution is unaffected by oxygen or copper salts.

Dimethylmalonic and succinic acids were briefly examined for comparison. They both behave similarly, as shown in Table I. The relative rates of decomposition in refluxing benzene (Figure 1) parallel increased bulk at the α carbon of the acid, indicating a steric basis for promotion of the decomposition. However, this conclusion must be tempered by the fact that these acids are involved in the decomposition itself, in contrast to malonic acid.^{3,4,10} This difference is evident in the increased yield of gas from the succinic acid precipitate. Also, work-up of the final mixture from decomposition of the dimethylmalonic acid precipitate afforded a small amount of sweet-smelling oil, probably 2,2-diacetoxyp propane.¹⁰ Neither of these decompositions produced well-defined precipitates which could be analyzed meaningfully.

The absence of oxygen inhibition, combined with the isomer distribution of the picolines produced in pyridine, thus point to a nonchain, free-radical decomposition of the mixed salt. Its insolubility precludes any significant attack by radicals in a potential chain-propagating step. In pyridine, exchange is apparently possible to yield pyridine-containing complexes which are even more labile than are the simple mixed salts. Therefore, whereas ethyl acetoacetate and other nonacidic materials may promote methylation by LTA because of the reactivity of an activated methylene group, the behavior of malonic acid must be attributed only to its ability to form a less stable, mixed salt. Other

dicarboxylic acids act similarly; the mode of decomposition, however, depends on the acid employed.

Experimental Section

Lead tetraacetate moist with acetic acid was placed in a tared flask which was then evacuated to a constant weight. Solvent was drawn into the flask instead of air until the LTA was covered, thus greatly reducing the sensitivity of dry LTA to atmospheric moisture. Pyridine reacts with LTA with evolution of heat to form a Pb(IV) complex. When it was used, the contents were allowed to return to room temperature. The flask was then opened to dry air or nitrogen and attached by means of Gooch tubing to a flask containing a known amount of solid acid. The other attachment was through a condenser either to a gas buret (total gas) or to a series of cold traps and weighed Ascarite tubes (CO₂). The whole apparatus was flushed with nitrogen before the acid was added; when measuring CO₂, the flow was continued throughout the run. The effect of oxygen was determined by measuring the rate of gas evolution after addition of a known amount of oxygen through a rubber septum. In some experiments, cuprous chloride was added during the run. No change in the rate of gas evolution was noted in either case.

In some experiments, the precipitate was collected in a drybox and dried to constant weight in a vacuum desiccator. It was used by adding it as quickly as possible to benzene at reflux temperature, care being taken to avoid excessive foaming.

Products were analyzed by vpc as individual fractions after fractional distillation of the filtered reaction mixture. Diphenyl ether was added to ensure complete distillation of picolines.

Precipitates were analyzed for lead by EDTA titration at pH 10, using Eriochrome T indicator,¹⁴ after digestion in hot nitric acid. The acetate to acid ratios were determined by nmr analyses of centrifuged water solutions obtained by treating the precipitates with excess sulfide ion.

Registry No.—Lead tetracetate, 546-67-8; malonic acid, 141-82-2; succinic acid, 110-15-6; dimethylmalonic acid, 595-46-0.

(14) H. Flaschka, A. J. Barnard, Jr., and W. C. Broad, *Chemist-Analyst*, **47**, 52 (1958).

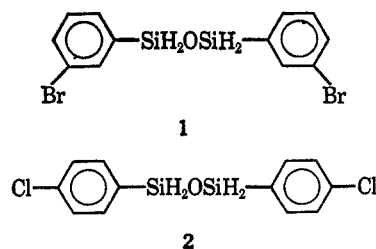
1,3-Bis(*m*-bromophenyl)- and 1,3-Bis(*p*-chlorophenyl)disiloxane

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We wish to report the synthesis of 1,3-bis(*m*-bromophenyl)disiloxane (1) and 1,3-bis(*p*-chlorophenyl)disiloxane (2) and an unusual redistribution reaction



which accompanies their hydrolysis. Only five 1,3-dialkylidisiloxanes^{1,2} and one diaryldisiloxane, 1,3-

(9) R. Daniels and O. L. Salerni, *Proc. Chem. Soc.*, 286 (1960).
 (10) J. J. Tufariello and W. J. Kissel, *Tetrahedron Lett.*, 6145 (1966).
 (11) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Amer. Chem. Soc.*, **64**, 2052 (1942).
 (12) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963).
 (13) J. K. Kochi, *ibid.*, **87**, 3609 (1965).

(1) H. H. Anderson and A. Hendifar, *J. Amer. Chem. Soc.*, **81**, 1027 (1959); H. H. Anderson, *ibid.*, **81**, 4785 (1959); H. H. Anderson, *ibid.*, **82**, 1323 (1960); H. H. Anderson and L. R. Grebe, *J. Org. Chem.*, **26**, 2006 (1961).
 (2) R. Müller, R. Köhne, and S. Sliwinski, *J. Prakt. Chem.*, **11**, 336 (1960).

diphenyldisiloxane,³ have been previously reported. Their hydrolytic behavior has not been studied.

The two disiloxanes were synthesized by the route used by Harvey, Nebergall, and Peake³ for 1,3-diphenyldisiloxane with critical modifications in procedure to compensate for the greater reactivity of the halophenyl compounds. Reduction of *p*-chlorophenyl- and *m*-bromophenyltrichlorosilane with lithium aluminum hydride proceeded smoothly, as reported for phenyltrichlorosilane,³ to give excellent yields of *p*-chlorophenylsilane^{4,5} and the previously unknown *m*-bromophenylsilane. Molecular weight determinations in acetone and benzene indicated *p*-chlorophenylsilane to be dimeric; however, the infrared and nmr spectra, both neat and in benzene solution, showed no abnormalities and were analogous to the spectra of *m*-bromophenylsilane which gave the expected value for molecular weight.

The conversion of *m*-bromophenyl- and *p*-chlorophenylsilane into the corresponding halophenylbromosilanes was accomplished by bubbling hydrogen bromide gas into an ethereal solution of the halophenylsilane at room temperature.^{3,6} Under these conditions, phenylsilane itself was converted into phenylbromosilane in almost quantitative yield with no evidence of further reaction of the product with hydrogen bromide after several hours. In contrast, vapor phase chromatograms of the reaction mixtures resulting from both *m*-bromophenyl- and *p*-chlorophenylsilane showed two higher boiling products in addition to the desired halophenylbromosilanes. Presumably, these were the halophenyldibromo- and -tribromosilanes formed by attack of hydrogen bromide on the initially formed product. In the case of *m*-bromophenylsilane, *m*-bromophenyldibromosilane was isolated by distillation and identified by elemental analysis; the suspected *m*-bromophenyltribromosilane was too thermally unstable to survive distillation. Acceptable yields of the desired halophenylbromosilanes were obtained by carefully monitoring the course of the reaction by gas chromatography and immediately distilling the reaction mixture when the optimum yield was reached.

Addition of ethereal solutions of the halophenylbromosilanes to ice, followed by immediate separation of the ether layer and distillation, afforded 1,3-bis(*m*-bromophenyl)disiloxane (1) and 1,3-bis(*p*-chlorophenyl)disiloxane (2) in yields of 74 and 86%, respectively. As a consequence of the electron-withdrawing halogen substituents,⁷ the bis(halophenyl)disiloxanes undergo facile hydrolysis. In contrast to 1,3-diphenyldisiloxane, which is not noticeably attacked in moist ether containing calcium sulfate,⁸ 1,3-bis(*m*-bromophenyl)- and 1,3-bis(*p*-chlorophenyl)disiloxane evolved hydrogen under these conditions and were consumed within 4 and 12 hr, respectively. With potassium carbonate in place of calcium sulfate, hydrolysis of the disiloxanes was complete within 10–15 min.

Hydrolysis, to give a siloxane polymer, was accompanied by partial rearrangement to the corresponding

halophenylsilane. The latter, formed in 23–27% yield based on halophenyl groups, were isolated from the calcium sulfate-catalyzed reaction by distillation and shown to be identical with authentic samples by refractive index, nuclear magnetic resonance and infrared spectroscopy, and vapor phase chromatographic retention time. The viscous polymer produced by calcium sulfate-catalyzed hydrolysis of 1,3-bis(*p*-chlorophenyl)disiloxane was not well characterized, although the presence of unhydrolyzed silicon–hydrogen bonds was indicated by infrared spectroscopy and by evolution of hydrogen upon treatment with sodium hydroxide. The resinous polymer obtained by hydrolysis in the presence of potassium carbonate, on the other hand, analyzed correctly for the fully hydrolyzed, cross-linked polymer, $(\text{ClC}_6\text{H}_4\text{SiO}_{1.5})_x$.

The rearrangement of the disiloxanes to halophenylsilanes apparently accompanies hydrolysis, since no rearrangement occurred with calcium sulfate or potassium carbonate in the absence of water. Furthermore, both hydrolysis and rearrangement proceeded in the absence of calcium sulfate or potassium carbonate in homogeneous water–tetrahydrofuran solution. It was also shown that the halophenylsilanes hydrolyze under the same conditions as the corresponding disiloxanes, but at a much slower rate.

Formation of the halophenylsilanes can be explained only by a redistribution of silicon–oxygen and silicon–hydrogen bonds. We know of only one other example of such a redistribution taking place under such mild conditions, that being with disiloxane itself, which has been reported to give monosilane upon hydrolysis,^{9,10} or monosilane and a solid residue upon storage at room temperature for long periods.¹¹ The mechanism of these redistributions is unknown.¹¹

Experimental Section¹²

Materials.—Tetrachlorosilane (Peninsular Chem-Research, Inc.) was redistilled before use, bp 57° (745 mm). *p*-Chlorophenyltrichlorosilane (Peninsular Chem-Research, Inc.) was used as received, 93% purity by gas chromatography. *m*-Dibromobenzene (Eastman Organic Chemicals), >97% pure by gas chromatography, was used as received.

***m*-Bromophenyltrichlorosilane.**¹³—*m*-Bromophenylmagnesium bromide was prepared from 29 g (1.2 g-atoms) of magnesium turnings and 236 g (1.0 mol) of *m*-dibromobenzene in 550 ml of ether. The resulting solution was diluted with 300 ml of ether and then added dropwise over a 3-hr period to a solution of 680 g (4.0 mol) of tetrachlorosilane in 1000 ml of ether while maintaining the mixture at 5–10° by means of an ice bath. The mixture then was allowed to warm to room temperature and stand overnight. The mixture was filtered in an atmosphere of dry nitrogen and the filter cake washed with ether. The combined filtrate was stripped of solvent and then distilled to obtain 112.3 g (39%) of *m*-bromophenyltrichlorosilane, bp 64–83° (0.20–0.35 mm).

Anal. Calcd for $\text{C}_6\text{H}_4\text{BrCl}_3\text{Si}$: C, 24.81; H, 1.39; Br, 27.51; Cl, 36.62; Si, 9.67; mol wt, 291. Found: C, 24.55; H, 1.38; Br, 27.76; Cl, 36.30; Si, 9.66; mol wt, 283.

(9) A. Stock and C. Somieski, *Ber.*, **56**, 132 (1923).

(10) These reactions are probably analogous to the sodium alkoxide-catalyzed redistribution of organoalkoxyasilane hydrides; ref 7, p 213.

(11) E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Co., New York, N. Y., 1963, pp 32–33.

(12) Boiling points are uncorrected. Infrared spectra were recorded both neat and in carbon disulfide on a Beckman IR-5 spectrophotometer. Nmr spectra were recorded in carbon tetrachloride on a Varian A-60 instrument using tetramethylsilane (δ 0) as an internal standard.

(13) E. J. Pepe, U. S. Patent 2,975,204 (Mar 14, 1961); *Chem. Abstr.*, **55**, 15,417 (1961). See, however, A. D. Petrov, M. I. Batuev, V. A. Ponomorenko, A. D. Snegova, A. D. Matveeva, and B. A. Sokolov, *Zh. Obshch. Khim.*, **27**, 2057 (1957).

(3) M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Amer. Chem. Soc.*, **79**, 1437 (1957).

(4) V. O. Reikhsfeld, *Zh. Obshch. Khim.*, **31**, 1576 (1961).

(5) A. M. Coleman and H. Freiser, *J. Amer. Chem. Soc.*, **83**, 4127 (1961).

(6) W. S. Miller, J. S. Peake, and W. H. Nebergall, *ibid.*, **79**, 5604 (1957).

(7) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, pp 200–207.

(8) As Drierite, W. A. Hammond Drierite Co., Zenia, Ohio.

Crude bis(*m*-bromophenyl)dichlorosilane, 35.9 g (17%), was obtained as a higher boiling fraction, bp 149–150° (0.12 mm); the crude product contained approximately 20% of close-boiling impurities which could not be removed by fractional distillation.

***m*-Bromophenylsilane.**—*m*-Bromophenyltrichlorosilane, 273.2 g (0.94 mol), in 175 ml of ether was added dropwise to 37.0 g (0.97 mol) of lithium aluminum hydride in 750 ml of ether at 10–15°. The mixture was allowed to warm to room temperature and stand overnight. Hydrolysis of the salts was effected by the addition of ice followed by 500 ml of cold 5% sulfuric acid. The ether layer was washed free of acid with cold water, separated and dried over anhydrous calcium sulfate.⁸ The ether was removed by distillation and the residual oil fractionally distilled to obtain 123.1 g (70%) of *m*-bromophenylsilane, bp 88.5° (29 mm), n_D^{25} 1.5652. Vapor phase chromatography indicated a purity of >99.5%. However, the material fumed in moist air and gave an immediate strong acid test with moist indicator paper indicating the presence of traces of acid impurities.

Characteristic bands in the infrared spectrum were noted at 3100, 2170, (Si–H),¹⁴ 2000–1650, 1600–1480, 1390 (Ar–Si),^{14,15} 1075, 995, and 920 (–SiH₃)¹⁶ cm⁻¹.

The nmr spectrum showed a singlet at δ –4.17 (Si–H; Si²⁹ satellites at –2.46 and –6.96, $J_{Si-H} = 203$ cps) and a multiplet centered at –7.32 (aromatic protons) in the ratio of 3.00:4.15.

Anal. Calcd for C₆H₇BrSi: C, 38.51; H, 3.77; Br, 42.71; Si, 15.01; mol wt, 187. Found: C, 38.72; H, 3.72; Br, 42.50; Si, 15.18; mol wt, 190.

***p*-Chlorophenylsilane.**^{4,5}—The lithium aluminum hydride reduction of 429 g (2.0 mol) of *p*-chlorophenyltrichlorosilane was carried out as described above for *m*-bromophenyltrichlorosilane. Distillation afforded 256.6 g (90%) of *p*-chlorophenylsilane, bp 75–77° (40 mm), n_D^{25} 1.5357 (lit.⁵ bp 76° (53 mm), n_D^{25} 1.5354). Vapor phase chromatography indicated a purity of at least 99.5%, although moist indicator paper showed an immediate acid reaction when exposed to an atmosphere of *p*-chlorophenylsilane suggesting the presence of traces of acid impurities.

The infrared spectrum exhibited characteristic bands at 3100–3025, 2170 (Si–H),¹⁴ 2000–1700, 1580–1490, 1390 (Ar–Si),^{14,15} 920 (–SiH₃),¹⁶ and 818 (*para* substituted) cm⁻¹.

The nmr spectrum had a singlet at δ –4.16 (–SiH₃; Si²⁹ satellites, $J_{Si-H} = 202$ cps) and a multiplet centered at –7.32 (aromatic protons, A₂B₂ symmetry) in the ratio of 3:4.

Anal. Calcd for C₆H₇ClSi: C, 50.51; H, 4.95; Cl, 24.85; Si, 19.69; mol wt, 143. Found: C, 50.42; H, 5.00; Cl, 24.47; Si, 19.83; mol wt, 288, 280 (osmometric in benzene and acetone, respectively).

***m*-Bromophenylbromosilane.**—Anhydrous hydrogen bromide gas was bubbled through a solution of 80.9 g (0.43 mol) of *m*-bromophenylsilane in 550 ml of ether for 6 hr at 15–20°. The course of the reaction was followed by gas chromatography and the reaction was stopped when only a trace of starting material remained. The ether and hydrogen bromide were immediately stripped at reduced pressure and the product distilled to obtain 83.6 g (73%) of crude product, bp 56–60° (0.20 mm). Redistillation gave 67.1 g (59%) of *m*-bromophenylbromosilane, bp 38–39° (0.06 mm).

Anal. Calcd for C₆H₆Br₂Si: C, 27.09; H, 2.27; Br, 60.08; Si, 10.56. Found: C, 26.99; H, 2.36; Br, 60.04; Si, 10.79.

When the reaction mixture, saturated with hydrogen bromide, was not worked up immediately, but was allowed to stand overnight, the yield of *m*-bromophenylbromosilane fell to 30%. The remainder of the product consisted of *m*-bromophenyldibromosilane, bp 66° (0.15 mm), isolated in 8% yield by distillation, as well as a higher boiling material which decomposed upon attempted distillation.

Anal. Calcd for C₆H₅Br₃Si: C, 20.89; H, 1.46; Br, 69.50; Si, 8.14. Found: C, 20.69; H, 1.60; Br, 69.60; Si, 7.97.

***p*-Chlorophenylbromosilane.**—Anhydrous hydrogen bromide was bubbled through a solution of 107 g (0.75 mol) of *p*-chlorophenylsilane in 750 ml of dry ether for 6 hr at 10–20°. The course of the reaction was followed by gas chromatography and gas introduction was stopped when only a trace of starting material remained. Ether and hydrogen bromide were removed as rapidly as possible at reduced pressure in the cold and the residual oil

was distilled to obtain 133.6 g (80%) of *p*-chlorophenylbromosilane, bp 46–50° (0.4–0.6 mm), n_D^{25} 1.5356.

Anal. Calcd for C₆H₆BrClSi: C, 32.52; H, 2.73; Br, 36.06; Cl, 16.00; Si, 12.66. Found: C, 32.37; H, 2.60; Br, 35.82; Cl, 16.05; Si, 12.49.

When the reaction mixture was not worked up immediately, but was allowed to stand in contact with hydrogen bromide, the yield of *p*-chlorophenylbromosilane dropped and two higher boiling materials appeared in the gas chromatogram of the reaction mixture. The higher boiling products could not be isolated by distillation in sufficient quantity and purity to permit an accurate analysis.

1,3-Bis(*m*-bromophenyl)disiloxane (1).—A solution of 67 g (0.30 mol) of *m*-bromophenylbromosilane in 200 ml of ether was shaken with ice, the ether layer immediately separated, and the ether was removed at reduced pressure. The residual oil was distilled¹⁷ to obtain 33.8 g (74%) of 1,3-bis(*m*-bromophenyl)disiloxane: bp 121–122° (0.05 mm); n_D^{25} 1.5916; d_{20} 1.5262. Vapor phase chromatography indicated the purity to be 97%.

The infrared spectrum showed absorbance at 3050, 2175 (Si–H),¹⁴ 2000–1700, 1570–1470, 1400 (Ar–Si),^{14,15} 1130–1075 and 950 (Si–O–Si),¹⁸ 920 and 870 (–SiH₂),¹⁶ and 780 cm⁻¹.

The nmr spectrum exhibited a singlet at δ –5.08 (–SiH₂–, Si²⁹ satellites, $J_{Si-H} = 225$ cps) and a multiplet centered at –7.39 (aromatic protons) in the ratio of 1:2, respectively.

Anal. Calcd for C₁₂H₁₂Br₂Si₂O: C, 37.12; H, 3.12; Br, 41.17; Si, 14.47; mol wt, 388. Found: C, 37.12; H, 3.27; Br, 41.33; Si, 14.70; mol wt, 398.

1,3-Bis(*p*-chlorophenyl)disiloxane (2).—A solution of 111.6 g (0.50 mol) of *p*-chlorophenylbromosilane in 325 ml of ether was shaken with 200 g of ice. The ether layer was immediately separated, the ether removed at reduced pressure, and the residue distilled to obtain 64.5 g (86%) of 1,3-bis(*p*-chlorophenyl)disiloxane: bp 117–115° (0.30–0.25 mm); n_D^{25} 1.5632; d_{20} 1.2033. Vapor phase chromatography indicated a purity of 97%.

The infrared spectrum had absorbances at 3100–3050, 2175 (Si–H),¹⁴ 2000–1750, 1600–1500, 1400 (Ar–Si),^{14,15} 1090 (Si–O–Si),¹⁸ 1022 (*para*-substituted), 955 and 850 (–SiH₂),¹⁶ and 815 cm⁻¹ (*para*-substituted).

The nmr spectrum had a singlet at δ –5.08 (Si–H; Si²⁹ satellites, $J_{Si-H} = 222$ cps) and a multiplet centered at –7.38 (aromatic protons, A₂B₂ symmetry); the ratio of silane to aromatic protons was 1:2.

Anal. Calcd for C₁₂H₁₂Cl₂Si₂O: C, 48.16; H, 4.04; Cl, 23.69; Si, 18.77; mol wt, 299. Found: C, 48.09; H, 4.22; Cl, 23.48; Si, 18.71; mol wt, 306.

Hydrolytic Redistribution of Bis(halophenyl)disiloxanes.—The hydrolysis of *m*-bromophenylbromosilane and *p*-chlorophenylbromosilane was carried out on a 0.2-mol scale as described above and the ethereal solutions were allowed to stand over calcium sulfate⁹ (1–2 g) for 24 hr. The calcium sulfate was removed by filtration, the ether was removed by distillation, and the oily residues were vacuum distilled to obtain 8.6 g (0.046 mol) of *m*-bromophenylsilane and 7.9 g (0.055 mol) of *p*-chlorophenylsilane, respectively. The products were identified by comparison of their refractive indices, nmr and infrared spectra, and vapor phase chromatographic retention times with those of authentic samples. The distillation residues consisted of clear, tacky, rubbery material which liberated hydrogen when treated with aqueous potassium hydroxide.

Test tube experiments (1 g of the disiloxane, 2 ml of ether, 0.5 g of calcium sulfate⁹ or potassium carbonate, and 0.5 ml of water) were monitored by vapor phase chromatography. These showed that the disappearance of 1,3-bis(*p*-chlorophenyl)disiloxane was complete in 10–15 min with potassium carbonate and in 12 hr with calcium sulfate. With 1,3-bis(*m*-bromophenyl)disiloxane, disappearance of the disiloxane was complete in 10–15 min with potassium carbonate and in 4 hr with calcium sulfate. Evolution of hydrogen, confirmed by mass spectrometric analysis, and formation of the corresponding halophenylsilanes paralleled the disappearance of the disiloxane.

The hydrolysate from the calcium sulfate-catalyzed hydrolysis of 1,3-bis(*p*-chlorophenyl)disiloxane was heated to 195° (0.3 mm) to drive off volatiles, leaving a clear, viscous material. The infrared spectrum showed characteristic absorption for Si–H at 2175 and Si–O–Si at 1088 cm⁻¹.

(14) M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Amer. Chem. Soc.*, **76**, 4555 (1954).

(15) C. W. Young, P. C. Servais, C. C. Currie, and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

(16) H. E. Opitz, J. S. Peake, and W. H. Nebergall, *ibid.*, **78**, 292 (1956).

(17) Pot residues were spontaneously flammable in air at room temperature.

(18) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

Anal. Calcd for $(\text{ClC}_6\text{H}_4\text{SiHO})_2$: C, 46.00; H, 3.22; Cl, 22.64; Si, 17.93. Found: C, 43.12; H, 3.25; Cl, 22.33; Si, 18.80.

The brittle resin from the potassium carbonate-catalyzed hydrolysis of 1,3-bis(*p*-chlorophenyl)disiloxane was triturated with ether and dried.

Anal. Calcd for $(\text{ClC}_6\text{H}_4\text{SiO}_{1.5})_2$: C, 44.04; H, 2.46; Cl, 21.66; Si, 17.17. Found: C, 43.81; H, 2.50; Cl, 20.97; Si, 17.07.

In the absence of water and using freshly dried samples of calcium sulfate and potassium carbonate, gas evolution was initially slow and stopped within 1 hr; only traces of halophenylsilane could be detected by vapor phase chromatography. Conversely, although 1,3-bis(*m*-bromophenyl)disiloxane gave no detectable reaction with water in the absence of calcium sulfate or potassium carbonate within 18 hr at room temperature, addition of sufficient tetrahydrofuran to give a homogeneous solution resulted in hydrogen evolution, formation of *m*-bromophenylsilane, and complete disappearance of the disiloxane in 3 days.

Similar experiments demonstrated that hydrolysis of *p*-chlorophenyl- and *m*-bromophenylsilane takes place at a much slower rate than with the disiloxanes. For example, 5-7 days were required for the complete disappearance of *m*-bromophenylsilane in the presence of calcium sulfate and water; only a trace of 1,3-bis(*m*-bromophenyl)disiloxane could be detected at any time in the mixture.

Registry No.—1, 15894-12-9; 2, 15894-13-0; *m*-bromophenyltrichlorosilane, 15894-14-1; bis(*m*-bromophenyl)dichlorosilane, 15894-15-2; *m*-bromophenylsilane, 15894-16-3; *p*-chlorophenylsilane, 3724-36-5; *m*-bromophenylbromosilane, 15894-18-5; *p*-chlorophenylbromosilane, 15894-19-6; *m*-bromophenyldibromosilane, 15894-20-9.

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Cyclic Ethylene Ketals of Chlorinated Cage Ketones. An Improved Synthesis of Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one¹

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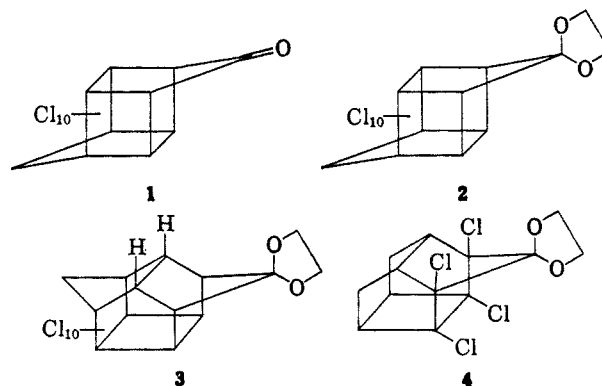
Ketalization is a valuable means for protecting ketone groups while other chemical transformations are carried out. However, conventional methods of ketal formation are not applicable to the highly electrophilic ketone (1), a strained chlorinated cage derivative. Thus Griffin and Price² found that 1 gave only hemiketals when treated with either ethyl orthoformate or ethylene glycol under the usual conditions for acid-catalyzed ketalization. These observations were explained by the destabilization, through angle strain and inductive effects, of the carbonium intermediate presumably involved in acid-catalyzed ketalization; it may be assumed that other strained α -halogenated ketones would be similarly resistant to normal ketalization procedures. Griffin and Price were able to make some full ketals of 1 by treating the hemiketals with diazomethane. The success of this

(1) A portion of this work has appeared as a preliminary communication: R. J. Stedman, L. D. Davis, and L. S. Miller, *Tetrahedron Lett.*, 4915 (1967).
(2) G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964).

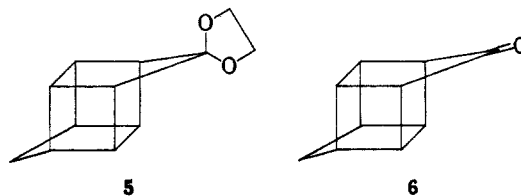
process depends on the stability and acidic character of the hemiketals of ketones of this type. We reasoned that these properties would enable us to prepare the cyclic ethylene ketals through base-catalyzed cyclization of the hemiketals formed by addition of a 2-haloethanol to the electrophilic carbonyl group. This approach has been used to prepare cyclic ketals of perfluoroacetone and related compounds.³

We found that 1 or its hydrate (which is presumably in equilibrium with a small concentration of the free ketone) reacted with 2-chloro- or 2-bromoethanol to give a hemiketal which, with triethylamine or aqueous sodium hydroxide, cyclized to the ketal 2 (Chart I). No cyclic ketal could be detected before treatment with base. The procedures given in the Experimental Section for the synthesis of 2 were selected from numerous preparative runs in which various combinations of the haloethanol and base components with either the ketone or its hydrate were successfully employed. The generality of the method was shown by preparing the ketals 3 and 4 from the corresponding ketones.

CHART I



Compound 2 was dehalogenated with lithium and *t*-butyl alcohol⁴ to give 5. Although there was extensive ring cleavage with formation of unsaturated by-products, a modest yield of 5 was readily isolated. Acid hydrolysis of 5 gave the ketone 6, the structure of which was confirmed by Wolff-Kishner reduction to the corresponding hydrocarbon. Although no strict comparison



under controlled conditions was made, the dechlorination of 2 appears to proceed more smoothly than that of the corresponding dimethyl ketal.² The sequence described here thus constitutes an improved route to the ketone 6.

Experimental Section⁵

Decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one, Cyclic Ethylene Ketal (2). Method A.—A mixture of 4.91 g (0.01

(3) H. E. Simmons and D. W. Wiley, *J. Amer. Chem. Soc.*, **82**, 2288 (1960).

(4) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).

(5) Corrected capillary melting points are reported. Infrared spectra were run in mull with a Perkin-Elmer Infracord; nmr spectra were run with a Varian A-60 spectrometer, at 5% concentration when solubility permitted, with TMS as internal standard.