Benzylation of III through Its Monopotassio Salt.—To a stirred suspension of 0.05 mole of potassium amide in 500 ml. of liquid ammonia was added 10.61 g. (0.05 mole) of finely powdered III, followed, after 0.25 hr., by 6.33 g. (0.05 mole) of benzyl chloride in 25 ml. of anhydrous ether. After stirring for 1 hr., the reaction mixture was worked up essentially as described previously to give 0.25 g. (2%) of N-benzyl-N,N'-diphenylurea (VI), m.p. 84–85°, and 9.65 g. (91%) of recovered III, m.p. 243–243.5°.

Attempted Benzylation of Certain Urea Compounds.—In Table I are summarized the results obtained on adding other urea compounds to two molecular equivalents of potassium amide in liquid ammonia, followed by one molecular equivalent of benzyl chloride. These experiments were performed essentially as described previously for that with the dipotassio salt of *sym*-diphenylurea (IV).

The urea compounds remained as precipitates after the water was added to the ethereal suspension of the reaction products, and were collected by suction filtration. Additional quantities of the urea compounds were precipitated and recovered by evaporation of the ethereal layers of the filtrates. The remaining oils were fractionally distilled *in vacuo* to give recovered benzyl chloride.

The urea compounds were identified by their melting points and by mixture melting points with authentic samples. The benzyl chloride was identified by comparison of its boiling point and refractive index with known values.

In the experiment with urea a purple color was observed during the addition of the benzyl chloride and no precipitate remained after the addition of water. The layers of the reaction mixture were shaken and separated. The ethereal layer was washed with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and the solvent removed. The oily residue was triturated with cold methanol, and the mixture filtered. The solvent was removed from the filtrate, and the residue was distilled *in vacuo* to give benzyl chloride. The remaining pot residue was recrystallized from methanol to give stilbene, which was identified by melting point and mixture melting point with an authentic sample.

The Preparation of (2,2-Dicarbethoxypropyl)ethoxydimethylsilane

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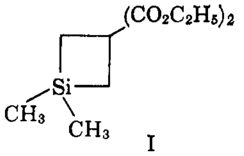
In connection with a program concerned with the preparation, properties, and reactions of small-ring organosilicon compounds, it became desirable to repeat the preparation of a compound previously designated as 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane (I). The preparation of this compound has been reported by several workers.[1,2] The general method utilized was a ring closure reaction of bis-(halomethyl)dimethylsilane and diethyl malonate effected with sodium alkoxide. In our work we employed the published procedure reporting the highest yield of this material.[2]

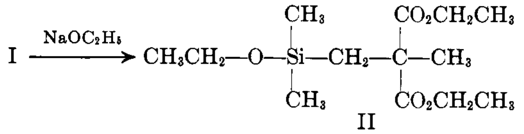
$$\mathrm{(CH_3)_2{-}Si{-}(CH_2X)_2 + H_2C(CO_2C_2H_5)_2 \xrightarrow{NaOR}}$$

$X = I^1$ or Cl^2
$R = CH_3{}^1$ or $C_2H_5{}^2$



I

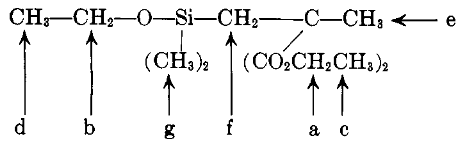
In our preparation a compound was obtained the properties of which were in excellent agreement with those previously reported.[1,2] The infrared spectrum of this material was shown to be superimposable with that of a known sample.[3] However, an examination of the n.m.r. spectrum of this material showed that it was not the previously reported silacyclobutane I, but rather a ring opened product, namely, (2,2-dicarbethoxypropyl)ethoxydimethylsilane (II). The formation of II can be explained in terms of a cleavage of I by sodium ethoxide.



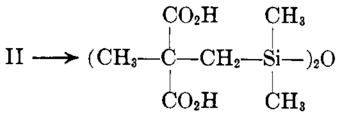
$$\mathrm{I} \xrightarrow{\mathrm{NaOC_2H_5}} \mathrm{CH_3CH_2{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_2{-}\overset{CO_2CH_2CH_3}{\underset{CO_2CH_2CH_3}{C}}{-}CH_3}$$

II

The n.m.r. spectrum of II contained a pair of quartets centered at 5.92 (J = 7.2 c.p.s.) and 6.42 τ (J = 7.2 c.p.s.) assigned to the protons a and b, respectively. The c and d protons appeared as a pair of triplets[4] centered at 8.78 (J = 7.2 c.p.s.) and 8.89 τ (J = 7.2 c.p.s.), respectively. The remainder of the spectrum consisted of singlets centered at 8.62, 8.81, and 9.92 τ assigned to the e, f, and g protons, respectively. The relative areas of all peaks were in agreement with the proposed structure.



It was previously reported[1] that the basic hydrolysis of I proceeded with ring opening to yield *sym*-bis-(2,2-dicarboxypropyl)tetramethyldisiloxane (III). Although the reactivity of other known silacyclobutanes[5–7] would predict such behavior for I, the above observation also can be explained in terms of our proposal. Thus, we have found that hydrolysis of II under similar conditions yields III. On the basis of the physical, chemical, and spectral evidence presented in this report it appears that the compound previously designated as 3,3-dicarbethoxy-1-silacyclobutane (I) is (2,2-dicarbethoxypropyl)ethoxydimethylsilane (II).



$$\mathrm{II} \longrightarrow (\mathrm{CH_3{-}\overset{CO_2H}{\underset{CO_2H}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}})_2\mathrm{O}$$

III

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(1) R. West, *J. Am. Chem. Soc.*, **77**, 2339 (1955).

(2) Incidental to the preparation of 4,4-dimethylsilacyclohexanone, R. A. Benkeser and W. E. Bennett [*ibid.*, **80**, 5414 (1958)] isolated a compound identical with that reported by Dr. West (ref. 1). Their identification was based on a comparison of physical constants with those reported in ref. 1.

(3) We wish to thank Dr. R. A. Benkeser for providing us with an infrared spectrum of this material. Dr. R. West informed us that unfortunately, due to a change in academic location, neither an authentic sample nor an infrared spectrum of his original material was available for comparison purposes.

(4) The pair of triplets overlapped giving rise to four peaks of unequal intensity.

(5) L. H. Sommer and G. A. Baum, *J. Am. Chem. Soc.*, **76**, 5002 (1954).

(6) L. H. Sommer, U. R. Bennett, P. G. Campbell, and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).

(7) W. H. Knoth, Jr., and R. V. Lindsey, Jr., *J. Org. Chem.*, **23**, 1392 (1958).

Experimental

Preparation of (2,2-Dicarbethoxypropyl)ethoxydimethylsilane (II).—Sodium, 7.3 g. (0.318 g.-atom), was treated with 100 ml. of absolute ethanol. To the cooled mixture was added 152.9 g. (0.954 mole) of diethyl malonate (200% excess). The mixture was then heated at reflux temperature as 25 g. (0.159 mole) of bis(chloromethyl)dimethylsilane[8] in 40 ml. of absolute ethanol was added slowly. Subsequent to refluxing for 24 hr., 100 ml. of ethanol was removed by distillation and replaced with 200 ml. of water. The mixture was extracted several times with ether and dried over sodium sulfate. Following the removal of solvent and excess diethyl malonate by distillation, there was obtained 28.5 g. (92.5%, based on the g.-atom of sodium employed) of product, b.p. 79–81° (0.25 mm.), n^{20}_D 1.4345, d^{20}_{20} 1.0101 [lit.[1] b.p. 141–143° (15 mm.), n^{25}_D 1.4318, d^{25}_4 0.997].

Anal. Calcd. for $C_{13}H_{26}O_5Si$: C, 53.80; H, 8.96; MD, 76.19. Found: C, 53.90, 54.09; H, 8.93, 8.72; MD, 74.96.

The infrared spectrum of II as a capillary cell contained the pertinent absorption bands shown in Table I.

TABLE I

THE INFRARED SPECTRUM OF II

Band position, μ	Intensity[a]	Characteristic[b,c]
3.35, 3.44	m, w	Aliphatic C–H
5.78	s	CO_2R
7.8	m	
8.0	m	Si–CH_3
8.2	s	CO_2R
8.50, 8.62	m, m	Possibly Si–alkyl
9.12, 9.27, 10.58	s, m, m	Si–O–C_2H_5
11.94, 12.67	s, m	Si–CH_3

[a] Letters indicate the relative intensities of absorption bands: s, strong; m, medium; w, weak. [b] L. J. Bellamy "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954. [c] A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

The reaction residue consisted of 3.5 g. of red oil. Distillation of this residue under reduced pressure gave small amounts of materials which were not investigated completely.[9]

Hydrolysis of II.—A mixture of 4.0 g. (0.1 mole) of sodium hydroxide, 5.0 g. (0.0172 mole) of II, and 50 ml. of ethanol was refluxed for 5 hr. The precipitated potassium salt was removed by filtration and the filtrate discarded. The crude potassium salt was dissolved in 10 ml. of warm water and made just acidic with concentrated hydrochloric acid. The acidified solution was extracted with four 30-ml. portions of ether and dried over sodium sulfate. Evaporation of the solvent gave a white solid which was taken up in ethyl acetate. Addition of petroleum ether (b.p. 60–70°) gave 1.76 g. (62%) of *sym*-bis(2,2-dicarboxypropyl)tetramethyldisiloxane (III), m.p. 133–135° dec. (lit.[2] m.p. 131–133° dec.).

The infrared spectrum of III as a potassium bromide pellet contained the pertinent absorption bands shown in Table II.

TABLE II

THE INFRARED SPECTRUM OF III

Band position, μ	Intensity[a]	Characteristic[b]
2.75 to 4.15	broad	CO_2H
5.76	s, s	CO_2H
7.8	m	
8.0	m	Si–CH_3
8.40	m	Possibly Si–alkyl
9.65	s	Si–O–Si
11.91, 12.35, 12.55	s, s, m	Si–CH_3

[a] See footnote *a* in Table I. [b] See footnotes *b* and *c* in Table I.

Acknowledgment.—This research was supported by the United States Air Force under Contract AF 33(616)-6463 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. The authors are grateful to Dr. R. King for determination of the n.m.r. spectrum and to Dr. G. Morris for aid in its interpretation.

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[8] We wish to express our thanks to Dr. R. N. Meals for providing us with this material.

[9] Earlier workers (see ref. 2) have reported the isolation of a material believed to be *sym*-tetramethyldi(2,2-dicarbethoxy)propyldisiloxane, b.p. 155–161° (0.05 mm.), n^{24}_D 1.4468. We isolated a small amount (*ca.* 0.5 g.) of material which on the basis of its physical constants [b.p. 140–142° (0.005 mm.), n^{20}_D 1.4500] and infrared spectrum (band at 9.55 μ indicative of the Si–O–Si linkage) may be this symmetrical siloxane.

Dibromination of Adamantane[1]

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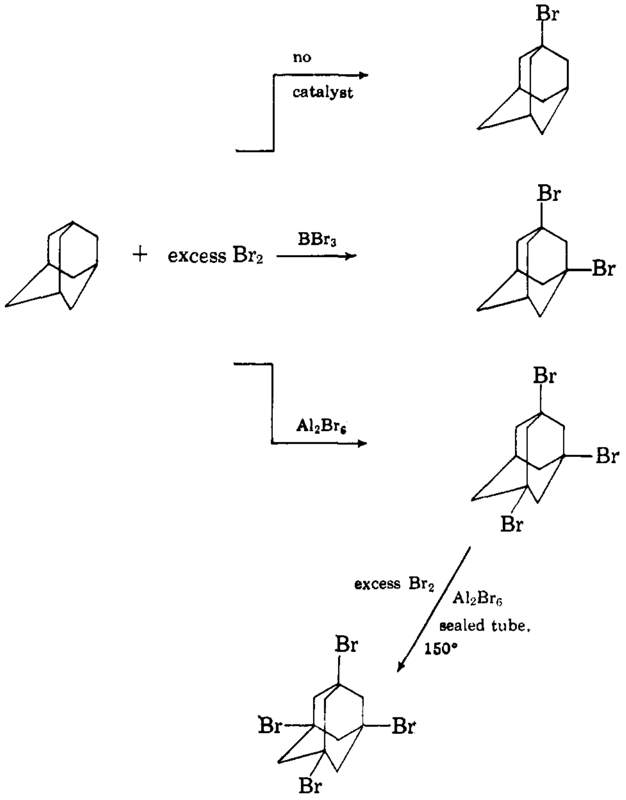
It has been reported that highly selective substitution on the adamantane ring system can be effected by bromination.[2,3] Thus, by the use of proper catalysts and conditions, one, two, three, or four bromine atoms can be inserted on the bridgehead sites.



Attempts in this laboratory to prepare the dibromosubstituted adamantane derivative using boron bromide as catalyst resulted in every case in the isolation of monobrominated adamantane in yields of 60 to 80%.

It was postulated that trace amounts of aluminum bromide may be necessary as cocatalyst since boron bromide can be made easily by a metathetical reaction

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[1] The semitrivial name "adamantane" has been used to designate the tricyclo[3.3.1.1^{3,7}]decane ring system.

[2] H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).

[3] H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960).