and slowly releasing the contents into the carbonation vessel. The argon flow was turned on following the complete evolution of the carbon dioxide. Elemental sulfur was then introduced into the reaction mixture in three or four portions (exothermic reaction). After 0.5 hr. of stirring at room temperature, water was added; the organic layer was separated, dried over sodium sulfate, concentrated, and distilled under reduced pressure to give the recovered phosphine (as the corresponding sulfide). The aqueous layer was acidified with hydrochloric acid and extracted thoroughly with ether. The ether extracts were combined, dried, and concentrated. The residue consisted of a mixture of either valeric acid or pivalic acid (if considerable amounts of these acids are present, it is necessary to remove them by high-vacuum distillation so that IV and V can be purified by crystallization), and IV–VI. The acids, IV and V, were purified by crystallization from a benzene–acetone mixture and a benzene–hexane mixture, respectively: IV, m.p. 195–198°[13]; and V, m.p. 120–122°. VI was esterified with methanol and distilled: b.p. 177–185° (0.2–0.25 mm.).

The organophosphines, I–III, were prepared by the reaction of chlorodiphenylphosphine, dichlorophenylphosphine, or dichloromethylphosphine with the corresponding Grignard reagents: I, b.p. 125–128° (0.5 mm.) [lit.[13] b.p. 108–110° (0.15 mm.)]; II, b.p. 85° (15 mm.) [lit.[14] b.p. 83–84° (13.5 mm.)]; and III, b.p. 110–120° (0.01–0.02 mm.), $n^{26}\mathrm{D}$ 1.4602. The dimethyldodecylphosphine, b.p. 107° (0.8 mm.), was prepared according to a described procedure.[15]

The organophosphine sulfides were prepared by the dropwise addition of the phosphines to a suspension of sulfur in benzene: methyldiphenylphosphine sulfide, b.p. 145° (0.015 mm.), $n^{27}\mathrm{D}$ 1.6506 [lit.[13] b.p. 162–163° (0.4 mm.), $n^{25}\mathrm{D}$ 1.6503]; dimethylphenylphosphine sulfide, m.p. 42.5–44.5° (lit.[16] m.p. 42°); and di-*n*-hexylmethylphosphine sulfide, b.p. 135–140° (0.02–0.03 mm.), $n^{26}\mathrm{D}$ 1.4967.

Di-*n*-hexylmethylphosphine oxide (very hygroscopic) was prepared by the oxidation of the corresponding phosphine with a slight excess of 15% hydrogen peroxide in benzene: b.p. 115–120° (0.04 mm.) [lit.[17] b.p. 130–135° (0.2 mm.)], m.p. 43–45° (sealed capillary).

Preparation of (Carboxymethyl)diphenylphosphine Sulfide (VI).—To a solution of 4.6 g. (0.02 mole) of methyldiphenylphosphine sulfide in 20 ml. of ether 0.022 mole of *n*-butyllithium was added dropwise. After 0.5 hr. of stirring, the reaction mixture was carbonated by pouring over an ether–Dry Ice slurry. Following the disappearance of the excess Dry Ice, the mixture was thoroughly extracted with water. Acidification of the aqueous extracts resulted in the separation of 2.35 g. (42%) of IV, melting over the range 189–193°. Two crystallizations from a benzene–acetone mixture (4:1) afforded 0.97 g. of IV, m.p. 192–195° (lit.[13] m.p. 193–195°).

Preparation of (Carboxymethyl)methylphenylphosphine Sulfide (V).—The V was prepared in the same manner as that described for IV; 6.3 g. (0.037 mole) of dimethylphenylphosphine sulfide, 0.04 mole of *n*-butyllithium, and excess carbon dioxide gave 2.01 g. (25%) of V, m.p. 120–122°, after crystallization from a benzene–hexane mixture.

Anal. Calcd.: mol. wt., 214. Found: mol. wt. (mass spectrometric), 214.

Preparation of (Carbomethoxymethyl)di-*n*-hexylphosphine Sulfide (VI).—The acid obtained from 7.4 g. (0.03 mole) of di-*n*-hexylmethylphosphine sulfide, 0.035 mole of *n*-butyllithium, and excess carbon dioxide was esterified using methyl alcohol in the usual manner to give 3.6 g. (39%) of product, $n^{26}\mathrm{D}$ 1.4943.

Anal. Calcd.: mol. wt., 306. Found: mol. wt. (mass spectrometric), 306.

Acknowledgment.—The authors wish to express their appreciation to Drs. C. D. Broaddus, R. G. Laughlin, and T. J. Logan for valuable discussions during the course of this investigation, to Mr. D. W. Bishop for aid in carrying out many of the reactions, and to Dr. J. H. Collins for the mass spectral analyses.

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[13] D. Seyferth and D. E. Welch, *J. Organometal. Chem.*, **2**, 1 (1964).

[14] J. Meisenheimer, J. Casper, M. Höring, W. Lauter, L. Lichtenstadt, and W. Samuel, *Ann.*, **449**, 213 (1926).

[15] R. G. Laughlin and J. T. Yoke, French Patent 1,317,586 (March 13, 1962).

[16] R. A. Zingaro and R. E. McGlothlin, *J. Chem. Eng. Data*, **8**, 226 (1963).

[17] J. J. Richard and C. V. Banks, *J. Org. Chem.*, **28**, 123 (1963).

Studies in the Benzosilacycloalkene Series. III. Reactions of (*o*-Chlorophenyl)alkyl Derivatives with Magnesium and Lithium

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Initiation difficulties were encountered in preparing Grignard reagents in tetrahydrofuran from aryl chlorides containing an *o*-alkyl group. Lithium reacted readily with these compounds, but with silicon-containing compounds cleavage reactions apparently occur. [3-(*o*-Chlorophenyl)propyl]triphenylsilane underwent a cleavage–cyclization reaction with molten sodium to give 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene.

Previous papers[1] from this laboratory described a method for the preparation of various silicon-substituted 2:3-benzo-1-silacycloalkenes by ring closure of (*o*-chlorophenyl)alkylsilanes with molten sodium in toluene. These compounds were subsequently converted into functional derivatives[2] which should serve as precursors to larger ring systems.

However, attempts to effect ring closure of dibenzyl-[2-(*o*-chlorophenyl)ethyl]- and dibenzyl-[3-(*o*-chlorophenyl)propyl]silane with molten sodium failed. Furthermore, when *o*-chlorobenzyldiphenylsilane was similarly treated, a 55.5% recovery of the starting material was realized. We then became interested in the ease of reaction of these *o*-chloro derivatives with not only sodium, but lithium and, particularly, magnesium in tetrahydrofuran. An intramolecular cyclization reaction of the Grignard reagent of (*o*-chlorophenyl)-alkylsilanes should prove useful for the preparation of Si-H-containing benzosilacycloalkenes.[3] Having on hand various other *o*-chlorophenylalkyl derivatives, their reactivity was investigated.

Tetrahydrofuran has been found to be a useful solvent for the preparation of Grignard reagents from aryl chlorides,[4] and Ramsden and co-workers[4b] were able to prepare a Grignard reagent from every aryl chloride tried (*o*-alkyl other than methyl- and ethylpentachlorobenzene were not reported), except 2-

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[1] (a) H. Gilman and O. L. Marrs, *Chem. Ind.* (London), 208 (1961); (b) H. Gilman and O. L. Marrs, *J. Org. Chem.*, **29**, 3175 (1964).

[2] H. Gilman and O. L. Marrs, *ibid.*, **30**, 325 (1965).

[3] See H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959), for a study of the reaction of Grignard reagents with silicon hydrides.

[4] (a) H. Normant, *Compt. rend.*, **239**, 1510 (1954); (b) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957); (c) H. E. Ramsden, U. S. Patent 2,838,508 (1958).

TABLE I

REACTIONS OF (o-CHLOROPHENYL)ALKYL DERIVATIVES IN TETRAHYDROFURAN

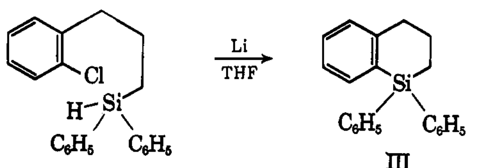
Run	Chloro compd.	Metal	Catalyst[a]	Initiation time	Total reflux time, hr.	Method of work-up	Product (yield, %)
1	[3-(*o*-Chlorophenyl)propyl]triphenylsilane[b]	Mg[c]	C_2H_5Br		24	Hydrol.	Starting material (60)
2	[3-(*o*-Chlorophenyl)propyl]triphenylsilane	Mg	C_2H_5Br	19 hr.	24	Hydrol.	3-Phenylpropyltriphenylsilane (65)
3	[3-(*o*-Chlorophenyl)propyl]diphenylsilane	Mg	I_2, C_2H_5I		3	Hydrol.	Starting material (85.4)
4	3-(*o*-Chlorophenyl)propyl bromide	Mg		5 min.	20	CO_2	4-(*o*-Carboxyphenyl)butyric acid (19.2)[d]
5	*o*-Chloropropylbenzene[e]	Mg	I_2, C_2H_5I		18	CO_2	Starting material (65)
6	*o*-Chloroethylbenzene[f]	Mg	I_2, C_2H_5I	6.5 hr.	8.5	CO_2	*o*-Ethylbenzoic acid (88)[g]
7	*o*-Chlorotoluene	Mg	I_2, C_2H_5I	2.5 hr.	9	CO_2	*o*-Toluic acid (83)
8	[3-(*o*-Chlorophenyl)propyl]dipherylsilane	Li		50 min.	1[h]	Hydrol.	Oils
9	[3-(*o*-Chlorophenyl)propyl]triphenylsilane[i]	Li			0.5 at room temp.; 2.5 at reflux	Hydrol.	Starting material (83.5)[j]
10	[3-(*o*-Chlorophenyl)propyl]diphenylsilane	Li		20 min.	0.5 at 0–5°; 18 at room temp.	Hydrol.	2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene (9.8)
11	*o*-Chloropropylbenzene	Li		5 min.	5 at 0–15°	CO_2	*o*-Propylbenzoic acid (17.3)

[a] Four or five drops of the halide or a crystal of iodine. In some cases these were added intermittently. [b] Run simultaneously with run 2. [c] Magnesium allowed to react with ethyl bromide prior to use. The Grignard reagent was decanted from the magnesium. [d] Crude yield was 48%. [e] Run under the same conditions as 6 and 7. [f] Run simultaneously with run 7. [g] In a repeat run, the reaction could not be initiated. [h] At ice-bath temperature. [i] In an ether–tetrahydrofuran mixture. [j] Polymorphic form was recovered. See discussion.

chloro-*p*-xylene in which the initiation was difficult. Also, it was found that *o*-chlorophenylphenylsilane would not react with magnesium in tetrahydrofuran.[5]

Therefore, it is not surprising that, when *o*-chlorophenylalkyl derivatives were allowed to react with magnesium in tetrahydrofuran (Table I), considerable difficulties were encountered in the initiation of the reaction. Qualitatively, it appears that, when the alkyl group is ethyl, propyl, or substituted ethyl or propyl, the initiation becomes more difficult (no difficulties were encountered in preparing *o*-tolylmagnesium chloride) and, in some cases, may not be initiated at all. If the reaction can be initiated, the conversion to the Grignard reagent proceeds to a satisfactory yield.

However, the formation of organolithium reagents from these compounds seems to be a facile reaction, but the stability of the organolithium derivative in this solvent is much lower[6] than the Grignard reagent. Also, in the case of (*o*-chlorophenyl)alkylsilanes, the lithium effects silicon–carbon bond cleavage.[7] For example, [3-(*o*-chlorophenyl)propyl]triphenylsilane (I) gave only unidentifiable oils, and [3-(*o*-chlorophenyl)propyl]diphenylsilane (II) gave only a 9.8% yield of the cyclization product, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (III).

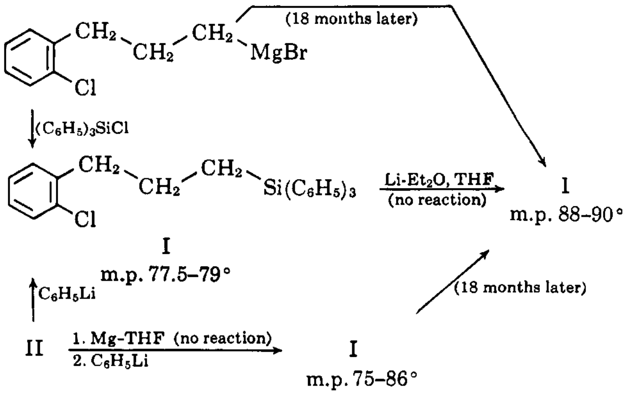


II → III

Unexpected results were obtained when [3-(*o*-chlorophenyl)propyl]triphenylsilane (I) was allowed to react with lithium in ether. Firstly, there was no apparent reaction even after the addition of tetrahydrofuran and refluxing of the mixture for 1 hr. Secondly, the recovered solid melted at 84–86°, about 9° above that of the starting material (I) which melted at 77.5–79°. The infrared spectra of the two compounds were superimposable. Compound I had been prepared by two methods (see Chart I) and was found to melt at 77–79°, but, when the recovered [3-(*o*-chlorophenyl)propyl]diphenylsilane (II) from the unsuccessful reaction of the silane with magnesium was treated with phenyllithium, the product melted over the range 75–86°. This material analyzed satisfactorily for I and the infrared spectrum was superimposable on that of the two forms melting at 77 and 84°.

When the preparation of I was repeated 18 months later, the product was observed to melt at 88–89°, even though the product had been seeded with the lower melting form. The melting point of the latter was rechecked and was found to melt over the range 77–87.5°. Also, the solid that had previously been observed to melt over the range 75–86° was found to melt at 89–90°. Again, the infrared spectra of these

CHART I



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[5] H. Gilman, E. A. Zuech, and W. Steudel, *J. Org. Chem.*, **27**, 1836 (1962).

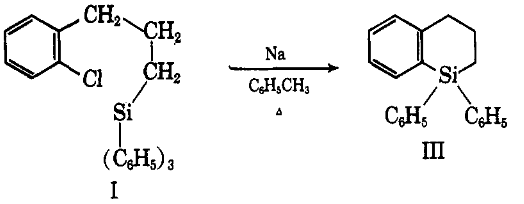
[6] H. Gilman and B. J. Gaj, *ibid.*, **22**, 1165 (1957).

[7] R. D. Gorsich, Ph.D. Thesis, Iowa State University, 1957.

derivatives were superimposable. This appears to be a case of polymorphism in which there is a slow transition from the lower melting form to the higher melting form. Attempts to reverse this process were unsuccessful.

Polymorphism has recently been observed with methoxytriphenylsilane,[8] *p*-tolyltriphenylsilane,[9] and 2-(N-ethyl-2,4-dibromoanilino)-5-bromophenyldiphenylsilanol.[10] In two of these cases,[8,10] attempts to convert the higher melting solid to the lower melting derivative were also unsuccessful.

Molten sodium in refluxing toluene usually reacts readily with these *o*-chloro compounds, as Clark, *et al.*,[11] coupled *o*-chlorophenyltrimethylsilane with chlorotrimethylsilane to give a good yield of *o*-phenylenebis(trimethylsilane), and the cyclization of (*o*-chlorophenyl)alkylsilanes affords good yields of the cyclic compounds. Exceptions were cited previously. Although I and lithium in tetrahydrofuran gave only oils, I and molten sodium in refluxing toluene underwent a cleavage–cyclization reaction to give the cyclic compound III. In all probability, [3-(*o*-sodiophenyl)-propyl]triphenylsilane is formed and then cyclizes with displacement of a phenyl group as phenylsodium.



I

III

Other cleavage–cyclization reactions with organosilicon compounds have been reported,[12] but these occurred when a five-membered cyclic silane was the product. Gelius[13] also obtained the five-membered ring compound 9,9-diphenyldibenzostannole from 2,2′-dilithiobiphenyl and triphenyltin chloride. However, when N-methyl-2,2′-dilithiodi-*p*-tolylamine was allowed to react with chlorotriphenylsilane,[14] the six-membered cyclic silane, 2,5,8-trimethyl-10,10-diphenyl-5,10-dihydrophenazasilane, was isolated. In this case phenyllithium was displaced.

Experimental[15]

[3-(*o*-Chlorophenyl)propyl]triphenylsilane. A. From Chlorotriphenylsilane. Run 1.—To an ethereal solution of chlorotriphenylsilane (10.3 g., 0.035 mole) was added 0.035 mole of 3-(*o*-chlorophenyl)propylmagnesium bromide.[1b] The mixture was refluxed overnight; Color Test I[16] was negative. Dilute hydrochloric acid was added and the organic layer was separated and dried. The concentrated oil was treated with petroleum ether (b.p. 60–70°) to give 1.0 g. (10.3%) of triphenylsilanol, m.p. and m.m.p. 149–152°. The filtrate was passed through a column of alumina. The eluate was distilled to give 4.38 g. (30.2%), b.p. 209–211° (0.015 mm.), and 1.23 g. (8.5%), b.p. 222° (0.016 mm.). The infrared spectra were superimposable, and the latter fraction was analyzed.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 6.92, 6.75.

These two fractions crystallized after 3 days to give long needles, m.p. 77.5–79°, after recrystallization from ethanol. Several months later this material melted over the range 77–87.5°.

Run 2.—When this reaction was repeated after 18 months, the petroleum ether filtrate was concentrated and treated with ethanol to give 5.03 g. (34%) of product, m.p. 84–86°. Recrystallization from ethanol raised the melting point to 88–89°.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 7.00, 6.98.

The infrared spectrum was superimposable with that of the previously prepared material.

B. From [3-(*o*-Chlorophenyl)propyl]diphenylsilane. Run 1.—An ethereal solution of phenyllithium (0.013 mole) was added to 4.24 g. (0.013 mole) of [3-(*o*-chlorophenyl)propyl]diphenylsilane (see below) in 10 ml. of ether. After refluxing 1 hr., the mixture was poured into an ammonium chloride solution. The organic layer was separated, dried, and concentrated. Recrystallization of the resulting solid from ethanol gave 2.3 g. (44.3%) of colorless crystals, m.p. 77.5–79.5°. A mixture melting point with an authentic sample of [3-*o*-chlorophenyl)propyl]triphenylsilane was not depressed. After 18 months this solid melted at 88.5–90°.

Run 2.—In a second run the recovered [3-*o*-chlorophenyl)-propyl]diphenylsilane (4.27 g., 0.013 mole) from the unsuccessful reaction with magnesium (run 3, Table I) was allowed to react with 0.013 mole of phenyllithium and then worked up as described above. The impure product, m.p. 70–73°, was recrystallized from ethanol to give 3.78 g. (72.1%) of product, melting over the range 75–86°. The infrared spectrum of the solid was superimposable on that of [3-(*o*-chlorophenyl)propyl]-triphenylsilane melting at 77.5–79 and 84.5–86.5°.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 6.78. The solid melted at 89–90° after some 18 months.

[3-(*o*-Chlorophenyl)propyl]diphenylsilane.—Compound II was prepared as was previously reported[1b] from 3-(*o*-chlorophenyl)-propylmagnesium bromide and chlorodiphenylsilane: b.p. 162–168° (0.005 mm.), $n^{20}{}_D$ 1.5923.

***o*-Chloroethylbenzene.**—*o*-Chlorobenzylmagnesium chloride (0.3 mole) was prepared from *o*-chlorobenzyl chloride and magnesium in ether and then alkylated with 0.6 mole of dimethyl sulfate according to the method used to prepare *n*-propylbenzene.[17] The yield of product, b.p. 81–84° (31 mm.), was 70.6%: $n^{20}{}_D$ 1.5219, $d^{20}{}_{20}$ 1.0595; lit.[18] $n^{20}{}_D$ 1.5218.

***o*-Chloropropylbenzene.**—*o*-Chlorobenzylmagnesium chloride (0.2 mole) was alkylated with diethyl sulfate as described in the previous experiment to give 23.1 g. (75%) of pure product, b.p. 70–71° (8.5 mm.), $n^{20}{}_D$ 1.5162, $d^{20}{}_{20}$ 1.0345.

Anal. Calcd. for $C_9H_{11}Cl$: C, 69.90; H, 7.17; MR_D, 45.25. Found: C, 69.04, 69.22; H, 7.15, 7.17; MR_D, 45.17.

Reaction of [3-(*o*-Chlorophenyl)propyl]triphenylsilane with Metals.—The following experiments are representative of those recorded in Table I.

A. With Magnesium.—A mixture of the silane (3.0 g., 0.0073 mole) and magnesium turnings in 20 ml. of tetrahydrofuran was refluxed 5 hr. at which time Color Test I was negative. Six drops of ethyl bromide was added and refluxing was continued 4 hr. Color Test I was still negative. However, after an additional 9 hr., the color test was positive. The mixture was refluxed 7 hr. and hydrolyzed. The aqueous layer was extracted with ether and discarded. The organic layer was dried, concentrated, and treated with a small amount of ethanol and a seed of 3-phenylpropyltriphenylsilane. There was obtained 1.74 g. (63.5%) of 3-phenylpropyltriphenylsilane, m.p. 65.5–67°, identified by mixture melting point with an authentic sample. Concentration of the mother liquor gave an oil.

In a second run, carried out simultaneously with the above, an excess of magnesium turnings was allowed to react with an ethereal solution of ethyl bromide, followed by removal of the Grignard reagent, to give a more active metal. A tetrahydro-

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[8] (a) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **82**, 3319 (1960); (b) A. G. Brook and H. Gilman, *ibid.*, **77**, 2322 (1955).

[9] B. J. Gaj, Ph.D. Thesis, Iowa State University, 1960.

[10] H. Gilman and E. A. Zuech, *J. Org. Chem.*, **26**, 3481 (1961).

[11] H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, **73**, 3798 (1951).

[12] (a) H. Gilman and R. D. Gorsich, *ibid.*, **80**, 1883 (1958); (b) D. Wittenberg and H. Gilman, *ibid.*, **80**, 2677 (1958).

[13] (a) R. Gelius, *Angew. Chem.*, **72**, 322 (1960); (b) *Ber.*, **93**, 1759 (1960).

[14] E. Gilman and E. A. Zuech, *J. Org. Chem.*, **27**, 2897 (1962).

[15] All melting and boiling points are uncorrected. Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. All solvents were pure and anhydrous.

[16] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[17] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 471.

[18] R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

furan solution of [3-(*o*-chlorophenyl)propyl]triphenylsilane, in the same quantities as used in the first run, was added to the magnesium, but after refluxing 24 hr. with intermittent additions of ethyl bromide, Color Test I was negative and the starting material was recovered in a 60% yield.

B. **With Lithium in an Ether–Tetrahydrofuran Mixture.**—A mixture of 3.48 g. (0.0084 mole) of [3-(*o*-chlorophenyl)propyl]-triphenylsilane and 0.7 g. (0.1 g.-atom) of cut lithium wire in 40 ml. of ether was stirred 30 min. at room temperature and then refluxed 1.5 hr. with no evidence of a reaction. Tetrahydrofuran (25 ml.) was added and the refluxing was continued 1 hr., but there was no change in the mixture. After acid hydrolysis, the aqueous layer was extracted with ether and discarded. The combined organic layer was dried and distilled to remove the solvents. Addition of ethanol to the residue gave 2.9 g. (83.4%) of a solid, m.p. 84–86°. The infrared spectrum of the solid was superimposable on that of the starting material, m.p. 77.5–79.5°. The melting point of the starting material was not depressed when the two solids were admixed. The solid was recrystallized twice from absolute ethanol and once from petroleum ether (b.p. 38–45°) to give fine needles, m.p. 84.5–86.5°.

Anal. Calcd. for $C_{27}H_{25}ClSi$: Si, 6.80. Found: Si, 6.86. The solid melted at 89.5–90° after 18 months.

Reaction of [3-(*o*-Chlorophenyl)propyl]diphenylsilane with Lithium.—To finely cut lithium wire (0.7 g., 0.1 g.-atom) in 50 ml. of tetrahydrofuran (THF) was added 30 ml. of a solution of [3-(*o*-chlorophenyl)propyl]diphenylsilane (14.5 g., 0.043 mole) in 50 ml. of the same solvent. The mixture was cooled to 0.5° and, after 20 min., a green color developed. The addition was completed during which time the color became deep red. After stirring 30 min. at this temperature, the solution was filtered through a glass-wool plug into a second flask. The mixture was stirred overnight. The THF was distilled and 100 ml. of dry toluene was added. Color Test I was negative after refluxing 1 hr. The reaction mixture was hydrolyzed by pouring into iced sulfuric acid. Ether was added, followed by the usual separation, drying, and concentration techniques. The residual material was distilled under reduced pressure to give 2.62 g. of an oil, b.p. 163–182° (0.007 mm.), which partially crystallized upon standing. Recrystallization from ethanol gave 1.27 g. (9.8%) of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, m.p. 75–77°, identified by mixture melting point with an authentic sample[1] and by comparison of the infrared spectra.

The distillation residue was taken up in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Cyclohexane eluted a trace of the cyclic compound, whereas benzene and ethyl acetate gave viscous, pale green oils which could not be purified further.

Reaction of [3-(*o*-Chlorophenyl)propyl]triphenylsilane with Sodium.—To a cold suspension of 0.23 g. (0.01 g.-atom) of sodium in 20 ml. of toluene was added 1.91 g. (0.005 mole) of [3-(*o*-chlorophenyl)propyl]triphenylsilane. Although a pink color developed, the reaction appeared to be slow; therefore, the mixture was refluxed 10 hr. and cooled. Ethanol was added and the solution was poured into iced hydrochloric acid. Ether was added and the organic layer was separated and dried. Removal of the solvents gave 1.43 g. of an oil which was dissolved in petroleum ether (b.p. 60–70°) and poured onto a column of alumina. The same solvent eluted 0.45 g. (32.4%) of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene, m.p. 78.5–80°, identified by a mixture melting point determination and by comparison of the infrared spectra. A mixture melting point with the starting material was depressed to 63°. Further elution of the column with benzene and ethyl acetate gave a viscous yellow oil which could not be purified.

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Conformational Analysis. XLIII. Stereochemical Studies in the Cyclobutane Ring System[1-3]

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The *cis* and *trans* isomers of 1,3-dimethylcyclobutane have been prepared by stereospecific synthesis and the earlier geometric assignments have been found to be reversed. The *cis* isomer is inferred to be of lower enthalpy. The *cis* and *trans* isomers of methyl 3-methylcyclobutanecarboxylate have been prepared by stereospecific reactions and equilibrated. The *cis* isomer predominates over the *trans* at equilibrium; $\Delta F°_{338}$ is 0.3 kcal./mole. The *cis*- and *trans*-dimethyl 1,3-cyclobutanedicarboxylates have been equilibrated and $\Delta F°_{338}$ favors the *trans* isomer by 0.1 kcal./mole. The greater stability of the *trans* isomer here appears to be due to dipole–dipole interactions.

While the conformational aspects of the cyclohexane ring have been studied in great detail, much less is known concerning rings of other sizes.[4] The present paper is concerned with some of the conformational properties of the cyclobutane ring. Cyclobutane has been shown by electron diffraction[5,6] and by spectroscopic and thermodynamic measurements[7] to be puckered. Presumably the relief in torsional strain which results from a modest amount of puckering outweighs the additional bond-angle distortion in the molecule required by this puckering. The chemically interesting consequences of this nonplanarity have been explored to only a very slight extent.[3,8] Scale models show that there are two kinds of positions in cyclobutane, somewhat analogous to the axial–equatorial positions in cyclohexane. If there are two substituents located 1,3 to one another on the cyclobutane ring, the *trans* isomer has an equatorial–axial (ea) arrangement, while the *cis* isomer may be either diequatorial (ee) or diaxial (aa). It would appear from models

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(1) Paper XLII: N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *J. Am. Chem. Soc.*, **87**, 1232 (1965).

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(3) A preliminary communication describing some of this work was published earlier: J. M. Conia, J. L. Ripoll, L. A. Tushaus, C. L. Neumann, and N. L. Allinger, *J. Am. Chem. Soc.*, **84**, 4982 (1962). Many of the conclusions herein were presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963.

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