after which Color Test I was negative. The reaction mixture was hydrolyzed with dilute acid and treated as previously described. There was obtained from the organic layer, a white solid which was recrystallized from petroleum ether (b.p. 60–70°) to give 5.1 g. (51%) of crystalline product melting at 159–161°.

Anal. Calcd. for $C_{108}H_{100}Si_5$: C, 84.31; H, 6.55; Si, 9.13. Found: C, 84.41, 84.43; H, 6.53, 6.43; Si, 9.07, 9.22.

The reactions of *p*-tribenzylsilylphenyllithium with tribenzylsilane and diphenyldichlorosilane were carried out in an analogous manner (Table II).

Acknowledgment. This research was supported in part by the United States Air Force under contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are also grateful to the Institute for Atomic Research, Iowa State University for the infrared spectra determinations.

AMES, IOWA

[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

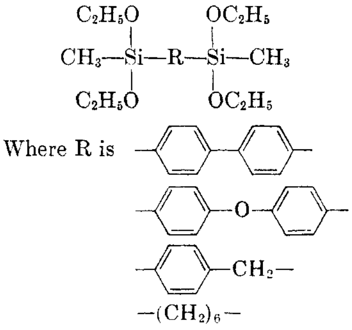
Synthesis of Bis(diethoxymethylsilyl) Derivatives of 4,4′-Dibromobiphenyl, 4-Bromophenyl Ether, α,*p*-Dibromotoluene, and 1,6-Dibromohexane[1]

L. W. BREED

Received January 15, 1960

The syntheses of bis-*p*-(diethoxymethylsilyl)phenyl ether, 4,4′-bis(diethoxymethylsilyl)biphenyl, 1,6-bis(diethoxymethylsilyl)hexane, and α,*p*-bis(diethoxymethylsilyl)toluene are described.

As a part of our continued interest in novel silane monomers for use in the preparation of cross-linked siloxane polymers, we have prepared a series of compounds with the following structure:


$CH_3-Si(OC_2H_5)_2-R-Si(OC_2H_5)_2-CH_3$

Although the synthesis of *p*-phenylenedisilanes was investigated earlier,[2] procedures for their preparation could not be extended to this series. For each of the new compounds it was necessary to find a method that would give pure materials in satisfactory quantities for evaluation studies.

Derivatives of 4,4′-dibromobiphenyl and p-bromophenyl ether. According to the literature, lithium and sodium reactions give 4,4′-disilyl derivatives of 4,4′-dibromobiphenyl and *p*-bromophenyl ether, but only the lithium derivatives have been used to prepare silane derivatives with hydrolyzable functionality. With dilithium intermediates Baum obtained 4,4′-bis(chlorodimethylsilyl)biphenyl and bis-*p*-(chlorodimethylsilyl)phenyl ether[3]; however, others have reported difficulty in repeating his procedure.[4] Various totally alkylated and arylated derivatives, also prepared *via* the dilithium intermediates, have been reported by Gilman.

By means of condensations in the presence of sodium, Clark prepared 4,4′-bis(trimethylsilyl)biphenyl, 4,4′-bis(dimethylphenylsilyl)biphenyl, and bis-*p*-(dimethylphenylsilyl)phenyl ether from the dibromides and the appropriate chlorosilanes, but reported no yields.[5]

Polymeric materials were the chief products when dilithium reagents were treated with polyfunctional silanes in our laboratory. Polyfunctionality of both reactants required inverse addition, but the dilithium derivative could not be transferred and added satisfactorily to the silane because it was a solid.

Although the bis-*p*-(diethoxymethylsilyl)phenyl ether was conveniently prepared by a condensation in ethyl ether in the presence of sodium, the corresponding derivative of 4,4′-dibromobiphenyl could not be prepared by the same method. The limiting factor was apparently the solubility of the dibromide whose concentration in solution was too low to permit the reaction to proceed at a satisfactory rate. Arylsodium intermediates were apparently formed in tetrahydrofuran, but were destroyed by the solvent. Only *p*-bromophenyl ether in ethyl ether provided adequate dibromide concentration to promote an exothermic reaction; the same reactants in toluene did not produce the con-

---

[1] This research was supported in whole or in part by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] L. W. Breed, W. J. Haggerty, Jr., and F. Baiocchi, *J. Org. Chem.*, in press.

[3] G. Baum, *J. Org. Chem.*, **23**, 480 (1958).

[4] R. L. Schaaf, P. T. Kan, and K. L. Rinehart, Jr., WADC Technical Report 58-187, Part II (1959); ASTIA Document No. 216451.

[5] H. A. Clark, U. S. Patent **2,628,242** (1953); Brit. Patent **671,553** (1952).

densation product. For these syntheses a rapid condensation was necessary because the reaction of coupling to form polysilanes could be expected to predominate if the initial reaction of sodium with the dibromide were slow.

No disilane derivates of biphenyl or phenyl ether, prepared from intermediate di-Grignard reagents, are reported in the literature, although several citations record the synthesis of the di-Grignard reagents.[6-8] Where experimental details are available, the di-Grignard reagent derivatives were prepared in yields of about 40% by entrainment of the dibromide in ethyl ether with either iodine or ethyl bromide.

In our laboratory, disilane derivatives were not obtained when the Grignard reagents, prepared by either entrainment procedure, were added to methyltriethoxysilane or to methylchlorodiethoxysilane, except in one case. When the Grignard reagent of *p*-bromophenyl ether, obtained by entrainment with ethyl bromide, was added to methyltriethoxysilane a mixture of the mono- and disilane derivatives was produced in low yield. As in the case of dilithium intermediate, the solid nature of the di-Grignard reagents offered difficulties in manipulation.

Both dibromides failed to form a Grignard reagent in ether under conventional conditions, in the presence or absence of the silane. In tetrahydrofuran, however, Grignardization of the dibromides appeared to proceed normally. After only two hours reflux of the reactants, titration of the mixtures produced by both dibromides indicated that 40% of the bromine atoms were present as Grignard reagents.

Through the di-Grignard intermediate of 4,4′-dibromobiphenyl in tetrahydrofuran, 4,4′-bis(diethoxymethylsilyl)biphenyl was obtained in a 23% yield. *p*-Biphenyldiethoxymethylsilane was also obtained in a 14% yield suggesting an interaction with the solvent, but substitution of dibutyl ether for toluene in this synthesis failed to change the proportion of the products. Although the Grignard reagent formed readily, forcing conditions were required to effect condensation with the silane. To obtain a product it was necessary to add the dibromide and silane to the magnesium concomitantly, replace the largest part of the solvent with toluene, and reflux the mixture overnight. If the product was filtered and distilled after a five-hour reflux period in tetrahydrofuran, the product was decomposed by uncondensed Grignard reagent during the distillation. Pouring such a mixture into water, however, gave the expected product, but in a lower yield. The yield of the disilylbiphenyl was not uniformly reproduced in replicate runs.

The necessity of using longer reaction times and higher reaction temperatures for the condensation of the di-Grignard reagent of 4,4′-dibromobiphenyl in tetrahydrofuran with chlorosilanes indicates that the product might also have been obtained by the various entrainment procedures had more vigorous conditions been used.

Derivatives of α-p-dichlorotoluene and 1,6-dibromohexane. 1,6-Bis(diethoxymethylsilyl)hexane was readily prepared by adding the intermediate di-Grignard reagent, prepared according to the method of Kreuchunas,[9] to a stirred solution of methyltriethoxysilane. Yields as high as 43% were obtained. Substitution of chlorodiethoxymethylsilane for methyltriethoxysilane in the synthesis gave a product whose empirical formula and neutralization equivalent corresponded to the product plus one equivalent of chlorine ($C_{16}H_{38}O_4Si_2Cl$). No structure was assigned to this compound.

The preparation of a silicon-functional 1,6-disilylhexane has been previously reported by Sveda.[10] He treated a mixture of magnesium and dichlorodimethylsilane in ether with 1,6-dichlorohexane to obtain 1,6-bis(chlorodimethylsilyl)hexane, but reported no yield.

The synthesis of *α,p*-bis(diethoxymethylsilyl)-toluene required a 2-step procedure. An attempt to prepare the diGrignard reagent of *α,p*-dichlorotoluene in tetrahydrofuran gave 4,4′-dichlorobibenzyl in a 46% yield.

p-Chlorobenzyldiethoxymethylsilane was obtained in a 70% yield when *α,p*-dichlorotoluene and chlorodiethoxymethylsilane were added concomitantly to magnesium in ether. The yield was substantially lowered when methyltriethoxysilane was substituted for chlorodiethoxymethylsilane. *p*-Chlorobenzyldiethoxymethylsilane was conveniently converted to *α,p*-bis(diethoxymethylsilyl)toluene by condensation with chlorodiethoxymethylsilane in the presence of sodium in refluxing toluene. The yield was about 70%.

EXPERIMENTAL

Unsuccessful attempts to couple dilithium reagents with various silanes. The dilithium derivative of 4,4′-dibromobiphenyl, prepared by the method of Gilman, *et al.*,[11] was a gummy solid adhering to the walls of the flask and the stirrer, and could not be transferred to a dropping funnel for addition to a silane.

The dilithium derivative *p*-bromophenyl ether, prepared according to the same procedure, was a grayish solid. Addition of the latter reagent to a stirred solution of methyltrichlorosilane or methyltriethoxysilane in benzene failed to yield any identifiable products. Distillation residues contained large quantities of resinous, nondistillable materials.

Unsuccessful attempts to condense 4,4′-dibromobiphenyl and p-bromophenyl ether with chlorodiethoxymethylsilane in the presence of sodium. When a stirred mixture of 13.0 g. of fused

---

[6] M. S. Malinovskii and V. M. Pokrovskii, *Trudy Gor'kov. Gosundarst. Pedogog. Inst.*, **1940**, No. 5, 51, *Khim. Referat. Zhur.* 4, No. 2, 45 (1941); *Chem. Abstr.*, **37**, 3077 (1943).

[7] H. R. Snyder, C. Weaver, and C. D. Marshall, *J. Am. Chem. Soc.*, **71**, 289 (1949).

[8] R. Gibert, *Compt. rend.*, **205**, 443 (1939).

[9] A. Kreuchunas, *J. Am. Chem. Soc.*, **75**, 3340 (1953).

[10] M. Sveda, U. S. Patent **2,561,429** (1946).

[11] H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940).

sodium and 50 ml. of refluxing toluene was treated with 20% of a solution containing 39.0 g. (0.125 mole) of 4,4′-dibromobiphenyl, 42.3 g. (0.25 mole) of chlorodiethoxymethylsilane and sufficient toluene to dissolve the dibromide, no exothermic reaction could be initiated even though the characteristic purple color developed. Neither could a reaction be initiated when *p*-bromophenyl ether was treated under similar conditions.

With ether as the solvent, 31.2 g. (0.10 mole) of 4,4′-dibromobiphenyl, 39.1 g. (0.20 mole) of chlorodiethoxymethylsilane, 11.5 g. (0.5 mole g.-atom) of sodium as 1 mm. diam. wire and 350 ml. ether were stirred at reflux for 24 hr. The mixture became pale purple, but none of the desired product was isolated when the product was filtered, stripped, and the residue distilled.

In the absence of solvent, a mixture of 6.0 g. (0.26 mole) of sodium and 25 ml. of chlorodiethoxymethylsilane, heated at 120° and stirred, was treated with about 5 ml. of a solution containing 16.4 g. *p*-bromophenyl ether in 25 g. chlorodiethoxymethylsilane. A brown coating formed on the sodium and no reaction could be initiated.

When a mixture of 120 ml. of tetrahydrofuran, 16.5 g. (0.05 mole) of 4,4′-dibromobiphenyl, 5.5 g. (0.2 g.-atom) of sodium as 1 mm. diam. wire, and 20 g. (0.1 mole) of chlorodiethoxymethylsilane was stirred, the customary deep blue-purple color developed and external cooling was required to maintain the temperature between 35–40°. The color gradually became gray, then red-purple when the reaction was no longer exothermic. The product was filtered with difficulty and the color dissipated on exposure to air. None of the desired disilane was recovered when the filtrate was distilled, but inspection of the filtration residue showed that all the sodium had been used.

Bis-p-(diethoxymethylsilyl)phenyl ether. In a 5-l. flask equipped with stirrer and condenser were placed 164 g. (0.5 mole) of *p*-bromophenyl ether, 195 g. (2.2 moles) of chlorodiethoxymethylsilane, 50.6 g. (2.2 g.-atoms) of 1 mm. diam. sodium wire, and 1375 ml. of anhydrous ether. Although a reaction began immediately and spontaneously, it was not so vigorous as to require external cooling. After 3 hr. it was necessary to heat and occasionally stir the mixture to maintain a gentle reflux. Reflux was continued an additional 20 hr., and then the product was stirred rapidly for 2 hr. When the product was filtered and fractionally distilled, bis-*p*-(diethoxymethylsilyl)phenyl ether was collected at 195°, 0.1 mm., n_{D}^{25} 1.5013, d_4^{25} 1.054. In six similar runs the average yield was 29.3%.

Anal. Calcd. for $C_{22}H_{34}O_5Si_2$: C, 60.78; H, 7.88; Si, 12.92; MR_{D} 121.4. Found: C, 60.57; H, 7.70; Si, 12.56; MR_{D} 121.5.

In smaller batches, for example with 0.1 mole of *p*-bromophenyl ether, 0.44 g.-atom of sodium wire, 0.22 mole of chlorodiethoxymethylsilane, and 550 ml. of ether, the reaction did not begin spontaneously. If this mixture was stirred rapidly and refluxed for 24 hr., however, the product was obtained in about the same yield. Larger pieces of sodium failed to give a product.

Attempted preparation of bis-p-(diethoxyphenylsilyl)phenyl ether. When 11.6 g. (0.5 g.-atom) of 1 mm. diam. sodium wire, 32.8 g. (0.1 mole) of *p*-bromophenyl ether, 46.2 g. (0.2 mole) of chlorodiethoxyphenylsilane, and 650 ml. of anhydrous ether were stirred at reflux for 14 hr., and the product was filtered and distilled at atmospheric pressure to remove the solvents, a residue was obtained that could not be crystallized. Distillation at 10^{-4} mm. in a Hickman still heated to 325° gave 6 g. of a product, n_{D}^{25} 1.5555, d_4^{25} 1.2398, which was apparently impure 4-bromophenyl 4′-(diethoxyphenylsilyl)phenyl ether.

Anal. Calcd. for $C_{22}H_{23}BrO_3Si$: C, 59.58; H, 5.24; Si, 6.33; MR_{D} 114.54. Found: C, 60.90, 60.74; H, 5.87, 5.89; Si, 7.64, 7.61; MR_{D} 114.90.

DiGrignard reagents of 4,4′-dibromobiphenyl and p-bromophenyl ether in ethyl ether. A reaction could not be initiated when a solution of the dibromide, methyltriethoxysilane, and diethyl ether was added to magnesium turnings.

In an entrainment procedure, 15.6 g. (0.05 mole) of 4,4′-dibromobiphenyl, 4.3 g. (0.175 g.-atom) of magnesium shavings, and 30 ml. of anhydrous ether were treated with a solution of 3.8 ml. (0.05 mole) of ethyl bromide at a rate that maintained gentle boiling. After the product was refluxed 20 hr., all the 4,4′-dibromobiphenyl had dissolved and two liquid phases remained in the reaction flask. This Grignard reagent was transferred under nitrogen to a dropping funnel and added dropwise to a rapidly stirred solution of 32 g. (0.19 mole) of chlorodiethoxymethylsilane in 100 ml. of toluene. A voluminous white precipitate formed almost at once. When the product was filtered and distilled at 1.0 mm., 2.9 g. of material was obtained boiling at 170–205°. There was evidence of decomposition during the distillation and the product darkened and solidified on several days' storage. Addition of a similar Grignard reagent to 30 g. (0.17 mole) of triethoxymethylsilane in 100 ml. toluene gave two liquid phases. A heavy white precipitate formed when the mixture was refluxed 2 hr., but no material was obtained in the expected boiling range when the product was filtered and distilled at reduced pressure.

A Grignard reagent was prepared from 0.1 mole of *p*-bromophenyl ether by the addition of a solution of the dibromide and ethyl bromide in ether to magnesium. Addition of this intermediate to chlorodiethoxymethylsilane gave 13.5 g. of a product that distilled between 180–205° at 1.5 mm. The product however, fumed on exposure to moist air and formed dark tarry materials on standing. Redistillation produced further decomposition. When a similarly prepared Grignard reagent was added to methyltriethoxysilane, and the product was filtered and distilled, 5.2 g. (12.5% as the disilane) of a product which boiled at 180–220° at 0.5 mm. was obtained. Analyses correspond to a mixture of 30% of the disilane and 70% of the monosilane.

Anal. Calcd. for 70% $C_{17}H_{21}BrO_3Si$ and 30% $C_{22}H_{34}O_5Si_2$: C, 55.5; H, 6.4; Si, 8.9. Found: C, 55.85, 56.04; H, 6.12, 6.10; Si, 8.72, 8.43.

In another entrainment procedure 7.5 g. (0.3 g.-atom) of magnesium turnings, 50 ml. of anhydrous ether, and 50 ml. of anhydrous benzene were treated with 25.4 g. (0.2 g.-atom) of iodine in small portions. When the reaction subsided, 31.2 g. (0.1 mole) of 4,4′-dibromobiphenyl and 53.4 g. (0.3 mole) of methyltriethoxysilane were added in one portion. The mixture, heated 48 hr. at reflux and hydrolyzed in an ice water–toluene mixture, did not yield any products boiling over 110° at 0.1 mm.

DiGrignard reagents of 4,4′-dibromobiphenyl and p-bromophenyl ether in tetrahydrofuran. The Grignard reagents, prepared by the usual procedure, formed without the application of external heat in tetrahydrofuran. Both gave a weakly positive Gilman Color Test I, and titration[12] of a hydrolyzed aliquot of each indicated that about 40% of the bromine atoms were converted to Grignard reagent in both reactions. When the Grignard reagent of *p*-bromophenyl ether was carbonated, the resulting acids, purified by solution in 10% sodium carbonate, filtration, and reprecipitation with dilute sulfuric acid, had a neutralization equivalent of 200. Calcd. for *p*-bromophenoxybenzoic acid, 293; for 4,4′-oxydibenzoic acid, 129.

Both Grignard reagents, cooled to 20° and treated with chlorodiethoxymethylsilane, failed to yield the corresponding disilanes, regardless of whether the reaction mixtures were purified by hydrolysis and distillation or by filtration and distillation.

4,4′-Bis(diethoxymethylsilyl)biphenyl. A previously activated mixture of 42 g. of 4,4′-dibromobiphenyl (recrystallized from toluene), 24.5 g. of (1.06 g.-atoms) magnesium turnings, and 160 ml. of tetrahydrofuran was treated with a solution of 83 g. (total 0.4 mole) of 4,4′-dibromobiphenyl,

---

(12) H. Gilman, H. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

135 g. (0.8 mole) of chlorodiethoxymethylsilane, and 800 ml. of tetrahydrofuran by dropwise addition over a period of 3 hr. The product was heated with slow stirring for 3 hr. and then refluxed overnight. After 1 l. of dry toluene was added, 1800 ml. of solvents were distilled from the mixture and heating was continued for 16 hr. Filtration, followed by removal of the solvents by distillation and filtration of precipitated solids, yielded a residue which gave 163 g. of crude product boiling 42–163° at 0.1 mm. on distillation. Fractional distillation of the crude product yielded 18.8 g. (14%) of *p*-biphenylyldiethoxymethylsilane boiling 131–132°, 0.3 mm., n_D^{26} 1.5470, d_4^{25} 1.076, and 37.5 g. (23%) of 4,4′-bis(diethoxymethylsilyl)biphenyl boiling 185–187°, 0.4 mm., n_D^{25} 1.5253, d_4^{24} 1.084.

Anal. Calcd. for $C_{17}H_{22}O_2Si$: C, 71.30; H, 7.74; Si, 9.81; MR_D 84.02. Found: C, 71.11; H, 7.65; Si, 9.71; MR_D 84.40.

Anal. Calcd. for $C_{22}H_{34}O_4Si_2$: C, 63.11; H, 8.19; Si, 13.42; MR_D 118.38. Found: C, 63.02; H, 8.12; Si, 13.32, 13.19; MR_D 119.63.

When the procedure was modified and the product was refluxed 5 hr. without the addition of toluene, purification by decanting the product into water gave only 6.3% of the disilane and 7.9% of the monosilane along with biphenyl, bromobiphenyl, and unchanged 4,4′-dibromobiphenyl. Purification of a similar run by simple filtration and distillation gave two immiscible phases in the distillation flask. The lower phase, which solidified on cooling, decomposed during an attempted distillation. The upper phase yielded only unchanged 4,4′-dibromobiphenyl.

The yields of the two products were lower when larger quantities were treated. Substitution of *n*-butyl ether for toluene in the procedure failed to decrease the proportion of *p*-biphenylyldiethoxymethylsilane in the product.

1,6-Bis(diethoxymethylsilyl)hexane. The Grignard reagent, prepared by the method of Kreuchunas,[9] from 7.3 g. (0.3 g.-atom) of magnesium turnings and 23 g. (0.1 mole) of 1,6-dibromohexane in 100 ml. of anhydrous ether, was transferred to a dropping funnel under an atmosphere of nitrogen, then added dropwise to a stirred mixture containing 33.8 g. (0.24 mole) of chlorodiethoxymethylsilane and 100 ml. of anhydrous ether that had been cooled to −30° in a Dry Ice–methanol bath. After the addition was complete, the mixture was refluxed 2 hr. When the product was filtered and fractionally distilled, a product weighing 8.1 g. was obtained at 105–106°, 0.1 mm. This material hydrolyzed to form an acid on contact with water and gave a positive Beilstein test.

Anal. Calcd. for $C_{16}H_{38}O_4Si_2Cl$: C, 49.75; H, 9.94; Si, 14.54; Cl, 9.18; neut. equiv., 386. Found: C, 49.71, 49.82; H, 9.94, 10.03; Si, 14.94, 14.68; Cl, 9.17, 9.11; neut. equiv., 385.

In a second experiment, the Grignard reagent was prepared and added to a solution containing 42.7 g. (0.24 mole) of methyltriethoxysilane and 100 ml. of anhydrous ether which was cooled to −10°. When the addition was complete 100 ml. of benzene was added, the ether was distilled, and the mixture was refluxed at 80° for 3 hr. The product, worked up in a similar manner, gave 10.6 g. (29.4%) of 1,6-bis(diethoxymethylsilyl)hexane boiling at 130° at 0.1 mm. n_D^{25} 1.4252, d_4^{25} 0.910. This product was unaffected by water and gave a negative Beilstein test.

Anal. Calcd. for $C_{16}H_{38}O_4Si_2$: C, 54.80; H, 10.92; Si, 16.02; MR_D 98.51. Found: C, 54.47, 54.63; H, 10.57, 10.77; Si, 15.89, 15.80; MR_D 95.58.

Repetition of this experiment using 244 g. (1 mole) of 1,6-dibromohexane gave 123 g. (42.5%) of the same product.

p-Chlorobenzyldiethoxymethylsilane. In a 5-l. flask were placed 24.3 g. (1.86 g.-atoms) of magnesium turnings and 25 ml. of a mixture containing 240 g. (1.49 moles) of α,*p*-dichlorotoluene, 262 g. (1.55 moles) of chlorodiethoxymethylsilane, and 850 g. of anhydrous diethyl ether. The reaction was initiated and the remainder of the reactants were added dropwise over a 3-hr. period. When addition was complete, 1300 ml. of toluene were added and the mixture was stirred at 35° for a total of 2 hr. The product was filtered and the filtrate stripped to remove solvents. During the concentration, more salts separated, and an additional filtration was required. The residue was fractionally distilled at 5 mm. and yielded 268 g. (70%) of *p*-chlorobenzyldiethoxymethylsilane boiling at 118–119°, n_D^{25} 1.4854, d_4^{25} 1.066.

Anal. Calcd. for $C_{12}H_{19}O_2SiCl$: C, 55.68; H, 7.40; Si, 10.85; MR_D 70.29. Found: C, 55.59; H, 7.59; Si, 10.85, 10.92; MR_D 69.66.

Repetition of the same procedure with 0.1 mole of α,*p*-dichlorotoluene and 0.12 mole of methyltriethoxysilane gave 4.8 g. (18.5%) of *p*-chlorobenzyldiethoxymethylsilane.

p-Chlorobenzyldiethoxymethylsilane was satisfactorily prepared in a yield of 63% in an experiment in which 0.1 mole of α,*p*-dichlorotoluene and 0.1 mole of chlorodiethoxymethylsilane were used and the crude reaction mixture poured over a water–toluene–sodium bicarbonate–ice mixture. All attempts, however, to effect purification by hydrolysis of a run based on 0.8 mole of α,*p*-dichlorotoluene yielded no product.

p-Bromobenzyldiethoxymethylsilane. In a similar procedure, 50 g. (0.24 mole) of *p*-bromobenzylchloride was treated with 7.1 g. (0.3 g.-atom) of magnesium turnings and 49 g. (0.3 mole) of chlorodiethoxymethylsilane to yield 31.1 g. (42.4%) of *p*-bromobenzyldiethoxymethylsilane boiling 124–128° at 3 mm., n_D^{25} 1.5027, d_4^{25} 1.216.

Anal. Calcd. for $C_{12}H_{19}BrO_2Si$: C, 47.51; H, 6.31; Si, 9.25; MR_D 73.13. Found: C, 48.35; H, 5.86; Si, 9.49; MR_D 73.59.

α,p-Bis(diethoxymethylsilyl)toluene. Thirty-six grams (1.57 g.-atoms) of sodium was placed in a 3-l. flask equipped with a dropping funnel, stirrer, reflux condenser, and thermometer and covered with 85 ml. of toluene and 22 g. of chlorodiethoxymethylsilane. The mixture was heated to reflux, then stirred at 600 r.p.m. with a 12 mm. diam. blade to disperse the sodium. Addition of 10 ml. of a solution containing 168 g. (0.65 mole) of *p*-chlorobenzyldiethoxymethylsilane, 110 g. (total, 0.78 mole) chlorodiethoxymethylsilane, and 320 ml. toluene, caused a dark blue color to develop at once, and the remainder of the reactants were added dropwise at a rate which maintained reflux (liquid temperature, 110–114°). When the addition was complete, the mixture was stirred under reflux an additional hour, cooled, and filtered. Solvents were stripped from the filtrate by downward distillation and the residue was combined with a similar product prepared from 100 g. (0.39 mole) of *p*-chlorobenzyldiethoxymethylsilane. When the combined residues were fractionally distilled at 0.1 mm., 256 g. (69.5%) of α,*p*-bis(diethoxymethylsilyl) toluene was collected between 122–124°, n_D^{24} 1.4665, d_4^{25} 0.996.

Anal. Calcd. for $C_{17}H_{32}O_4Si_2$: C, 57.26; H, 9.05; Si, 15.76, MR_D 99.81. Found: C, 57.25; H, 8.84; Si, 15.76, 15.66; MR_D 99.33.

Unsuccessful Grignard reaction of α,p-dichlorotoluene in tetrahydrofuran. In a 500-ml. flask were placed 5.5 g. (0.22 g.-atom) of magnesium turnings and a sufficient portion of a mixture containing 16.1 g. (0.1 mole) of α,*p*-dichlorotoluene, 33.8 g. (0.2 mole) of chlorodiethoxymethylsilane, and 50 g. of tetrahydrofuran to cover the magnesium was added. The reaction was initiated and the remainder of the mixture was added at a rate to maintain the reaction. When the addition was complete, stirring was commenced and the mixture was heated at the reflux temperature for 3 additional hr. The product, filtered and poured over a mixture containing 100 g. of water, 100 g. of toluene, 15 g. of sodium bicarbonate, and ice, was separated and washed four times with 100-ml. portions of water, and dried over Drierite. On distillation, 5.8 g. of *p,p*′-dichlorobibenzyl (46.4%) was obtained boiling at 160° at 0.1 mm., and melting at 97–99° (from alcohol).

Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.94; H, 4.82. Found: C, 67.08; H, 4.89.

Acknowledgment. The author is indebted to Mr. Fred Baiocchi who verified many of the original observations by repetition of the experiments, and also performed the lithium syntheses.

KANSAS CITY 10, MO.

[CONTRIBUTION FROM THE AERONAUTICAL RESEARCH LABORATORY, WRIGHT AIR DEVELOPMENT DIVISION, AIR RESEARCH AND DEVELOPMENT COMMAND]

Urea Complexes of Partially Fluorinated Esters[1]

JACK RADELL AND JOSEPH W. CONNOLLY

Received November 24, 1959

The effect of fluorine on the ability of a partially fluorinated unbranched ester to form a urea channel complex was found to be predominantly steric and not polar. Complex formation depended upon the number of unfluorinated chain atoms referred to as anchor length and upon the location of the anchor in either the alkyl or acyl moieties of the ester. Knowing the anchor length of the shortest homologue forming a complex, the conformational analysis of an immobilized ester trapped in the prism of urea was determined. The x-ray powder diffraction data were used to determine the presence of urea complexes by indicating the presence of tetragonal urea, hexagonal complex, or a mixture of both. The most stable complexes showed no interplanar spacings for tetragonal urea. The less stable complexes partially dissociated giving characteristic spacings for urea and complex.

Because 2,2-difluorooctane forms a urea complex, the presence of two fluorine atoms upon a single carbon atom in a linear chain does not prevent complex formation.[2] Whether two or more fluorinated carbon atoms linked together in the chain would likewise permit complexing is not known.

EXPERIMENTAL

All complexes were prepared[3] by adding 30 drops of the sample[4] to 4.5 ml. of urea-methanol solution (0.15 g. urea/ml. of methanol) in a test tube. The tube was stoppered and shaken for 30 seconds and allowed to stand at 4° for 24 hr. The crystals that formed were filtered with suction and washed with 10 ml. of absolute ethanol at 4°. The product was vacuum-dried at 4° (1 mm.) over anhydrous calcium chloride for 24 hr. No crystals formed when the urea-methanol solution was used as a blank. In some cases tetragonal urea crystallized from the urea-methanol solution after a noncomplex forming compound had been added.

The dried urea complexes were finely ground with a mortar and pestle and applied to the surface of a roughened glass slide. The interplanar spacings and relative intensities were obtained using the Norelco X-ray diffractometer with a Geiger tube detector at 35,000 volts and 15 milliamps with a scanning rate of 1° per min. A General Electric recorder was used to obtain the data.

The following normal fluorinated acids and alcohols failed to form a complex: CF_3COOH, C_2F_5COOH, C_3F_7COOH, $C_5F_{11}COOH$, $C_7F_{15}COOH$, $C_9F_{19}COOH$, CF_3CH_2OH, C_3F_7-CH_2OH, $H(CF_2)_2CH_2OH$, $H(CF_2)_4CH_2OH$, $H(CF_2)_6CH_2OH$, $H(CF_2)_8CH_2OH$ and $H(CF_2)_{10}CH_2OH$. From this and the knowledge of which partially fluorinated esters will form complexes, one may conclude that esters of perfluoro acids with either α,α-dihydroperfluoro alcohols or α,α,ω-trihydroperfluoro alcohols will not form a complex; no members of either aforementioned class of hydroperfluoro alcohols, or perfluoro acid formed a complex.

From Table II it can be determined which compounds formed a pure complex, which caused the crystallization of pure urea, and which complexes partially dissociated giving the characteristic patterns of both. The compounds present in Table I and missing from Table II produced no crystalline material under complexing conditions.

In each series of esters where two homologues caused urea only to crystallize, the anchor lengths for the two esters were one and two less, respectively, than the minimum anchor length required for complex formation in that series. The shorter of the two caused the deposition of less urea. In all cases complexes of the higher homologues showed no evidence for dissociated urea which has a characteristic interplanar spacing line in the interval 4.00 to 4.04 Å. This line is most useful because it is relatively strong and does not occur in the x-ray powder diffraction patterns of any of the complexes. The most characteristic line for the urea complexes occurs between 4.11 and 4.17 Å. Other interplanar spacings useful for characterizing a urea complex appear at 3.55–3.64 Å and 7.13–7.19 Å. These spacings show a greater variation in intensity than does the 4.11–4.17 Å spacing. In a homologous series forming urea complexes the relative intensity of the 3.55–3.64 Å and 7.13–7.19 Å shows, in general, a gradual increase as the anchor length of the complexed molecule increases. This same trend[3] is observed for the urea complexes of alkylsilanes.

All measured cross-sectional diameters are maximum values of the planar zigzag conformation obtained from Stuart-Briegleb molecular models. This maximum is less than the maximum obtained from any other configuration.

DISCUSSION

The cross-sectional diameter of the fluorinated monoesters (Series II–VI, Table I) is 5.6 Å compared to 4.8 Å for the corresponding unfluorinated esters, because the effective radius of fluorine (1.3 Å) is 1.3 times greater than hydrogen (1.0 Å). The correspondingly bulkier fluorinated ester would be expected to form a less stable urea com-

---

[1] Presented before the International Symposium on Fluorine Chemistry in Birmingham, England, July 14–17, 1959.

[2] W. J. Zimmershied, R. A. Dinerstein, A. W. Weitkamp, and R. F. Marschner, *Ind. Eng. Chem.*, **42**, 1300 (1950).

[3] J. Radell and P. D. Hunt, *J. Am. Chem. Soc.*, **80**, 2683 (1958).

[4] The preparation of these compounds will be described in a separate publication.