denced by its visible spectrum. The color gradually faded as the phenoxy radical reacted with *N*-phenyl-2-naphthylamine. On the other hand, the 2,4-di-*tert*-butyl-4-methylphenoxy radical disproportionates[48] rapidly, and reversibility is not detected. From the second-order rate constant of Stebbins and Sicilio,[48a] the estimated half-life at 24° of a $10^{-3}$ *M* solution would be about 2 sec. In the presence of oxygen, the yield of AH from 2,4,6-tri-*tert*-butylphenol is nearly doubled as the reverse reaction is prevented by rapid scavenging of the phenoxy radicals by oxygen to form the peroxide which is stable at 60°.[49] As discussed earlier, A· is stable toward oxygen. The result in oxygen indicates that 2,4,6-tri-*tert*-butylphenol is only slightly less reactive than 2,6-di-*tert*-butyl-4-methylphenol, in agreement with kinetic data for reactions of peroxy radicals with these two phenols.[36a,50]

### Experimental Section

Preparations of compounds **1–5** have been described.[12,13] Products **11–13** were gifts of K. U. Ingold of the National Research Council of Canada.[19] Analytical procedures have been published.[13,19] For the determination of small amounts of **3** in the presence of excess **2**, it was necessary to develop the thin layer chromatogram in a tank saturated with water vapor.

**Acknowledgment.** The author is grateful to Dr. K. U. Ingold for helpful discussions and for the disclosure of experimental results prior to publication.

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(49) C. D. Cook and M. Fraser, *J. Org. Chem.*, **29**, 3716 (1964).

(50) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 2800 (1963).

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# Acid-Catalyzed Isomerization of 1,2-Bis(trimethylsilyl)benzene and Related Compounds

**Dietmar Seyferth* and David L. White**

*Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.* *Received July 24, 1971*

**Abstract:** When heated to about 152° in the presence of a few mole per cent of trifluoroacetic acid, 1,2-bis(trimethylsilyl)benzene isomerizes rapidly to a mixture containing mostly 1,3-bis(trimethylsilyl)benzene and a small amount of the 1,4 isomer. 1-Dimethylsilyl-2-trimethylsilylbenzene and 1,2-bis(dimethylsilyl)benzene undergo this isomerization as well, but to a much lesser extent. With 1-trimethylsilyl-2-trimethylgermylbenzene only 5% isomerization occurs, and 1,2-bis(trimethylgermyl)benzene isomerizes hardly at all. The rapid isomerization of 1,2-bis(trimethylsilyl)benzene is attributed to acceleration due to the steric strain resulting from nonbonded interactions between the two vicinal $Me_3Si$ groups. The lack of isomerization of 1,2-bis(trimethylgermyl)benzene apparently is due to the consumption of the acidic catalyst in Ge–C bond cleavage at a rate faster than that of the isomerization reaction. A mechanism for the isomerization process is proposed which involves protonation of the benzene ring, silyl group migration in the protonated intermediate, and finally deprotonation. This appears to be an equilibrium process, but the isomerization rates of the 1,3 and 1,4 isomers are very much slower.

In previous work, we demonstrated that the formation of 1,3-bis(trimethylsilyl)benzene in the Diels–Alder reaction of α-pyrone with bis(trimethylsilyl)acetylene in bromobenzene in a sealed tube was due to isomerization of the initially formed 1,2-bis(trimethylsilyl)benzene by acidic impurities present in the reaction mixture.[1] The acids most likely involved were HBr (from bromobenzene pyrolysis during sealing of the tube) or $H_2SO_4$ (from an α-pyrone preparation step). Addition of triethylamine to the reaction mixture prevented the isomerization, and 1,2-bis(trimethylsilyl)benzene then was the sole product. Other experiments showed that catalytic amounts of trifluoroacetic or *p*-toluenesulfonic acids catalyzed the isomerization of 1,2-bis(trimethylsilyl)benzene as well. Since 1,2 shifts of silyl substituents on aromatic rings had not been described previously, we felt that reactions of this type merited further study.

## Results and Discussion

The acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene was studied using 0.5 *M* benzene solutions of the silicon compound containing 2.3 or 5.0 mol % of trifluoroacetic acid. The samples were heated in sealed tubes for measured periods of time and then analyzed by gas–liquid partition chromatography (glc). Relative amounts of each isomer, as well as of trimethylphenylsilane (the product of acid desilylation), were determined. In addition, random samples were subjected to quantitative glc analysis to check the stoichiometry of the reaction. At room temperature the rate of isomerization was extremely slow (1% isomerization after 240 hr in the presence of 5 mol % $CF_3COOH$), and these isomerization experiments therefore were carried out at 152 ± 2°.

When 1,2-bis(trimethylsilyl)benzene was heated in benzene at 152° in the presence of 2.3 mol % $CF_3COOH$, its relative concentration fell exponentially to 2% in 48 hr. At the same time, the concentration of the 1,3 and 1,4 isomers rose to 93 and 5%, respectively. There was little further change with time (Figure 1). The effect of small amounts of trifluoroacetic acid on 1,3- and 1,4-bis(trimethylsilyl)benzene also was examined. The 1,3 isomer, under these conditions, rearranged only gradually to give (after 96 hr) a mixture containing 97% of the starting 1,3 compound and 3%

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(1) D. Seyferth and D. L. White, *J. Organometal. Chem.*, **34**, 119 (1972).

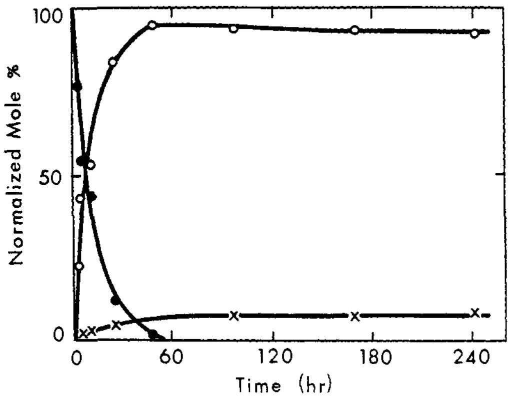


Figure 1. Isomerization of 1,2-bis(trimethylsilyl)benzene in benzene solution in the presence of 2.3 mol % $CF_3CO_2H$ at 152°: 1,2- (●), 1,3- (○), and 1,4-$(Me_3Si)_2C_6H_4$ (×).

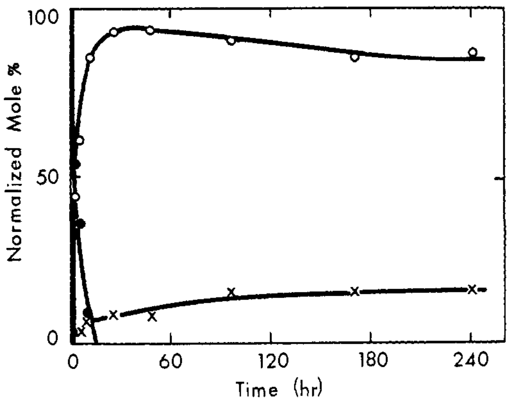
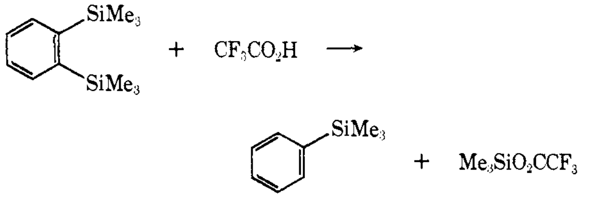


Figure 2. Isomerization of 1,2-bis(trimethylsilyl)benzene in benzene solution in the presence of 5.0 mol % $CF_3CO_2H$ at 152°: 1,2- (●), 1,3- (○), and 1,4-$(Me_3Si)_2C_6H_4$ (×).

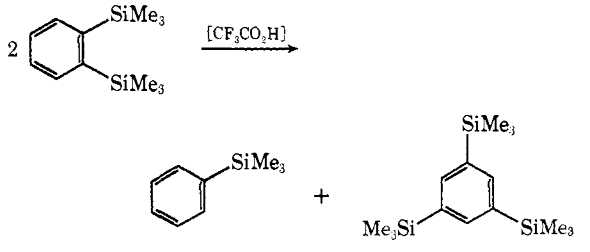
of 1,4-bis(trimethylsilyl)benzene. No 1,2-bis(trimethylsilyl)benzene was detected. 1,4-Bis(trimethylsilyl)benzene also isomerized very slowly in the presence of 3.8 mol % of $CF_3COOH$ at 152° in benzene solution, giving, after 96 hr, a mixture of 93.5% 1,4- and 6.5% 1,3-bis(trimethylsilyl)benzene.

When higher concentrations of trifluoroacetic acid were used in these experiments, the rate of isomerization of 1,2-bis(trimethylsilyl)benzene was greater (Figure 2). The isomerization rates of the 1,3 and 1,4 isomers also were accelerated when 5 mol % of trifluoroacetic acid was used. Within 96 hr, 9% of the 1,3 isomer had isomerized to the 1,4 compound. Using 8.6 mol % of $CF_3CO_2H$, 19% of the 1,4 isomer isomerized to 1,3-bis(trimethylsilyl)benzene during a reaction time of 96 hr at 152°.

The formation of trimethylphenylsilane in these experiments has been noted. When 2.3 mol % of trifluoroacetic acid was used, 4–14% of the bis(trimethylsilyl)benzene isomer charged was converted to $Me_3SiPh$; at higher acid concentrations, these conversions were higher, 16–32%. The formation of trimethylphenylsilane could have occurred either *via* simple trimethylsilyl cleavage by $CF_3CO_2H$ (eq 1) or by acid-catalyzed disproportionation of 1,2-bis(trimethylsilyl)benzene, eq 2. Careful glc examination of reaction mixtures failed to provide evidence for the presence of a tris(trimethylsilyl)benzene, and, specifically, 1,3,5-tris(trimethylsilyl)benzene, an authentic sample of which was available, was absent. On the other hand, trimethylsilyl trifluoroacetate was found to be present in these reaction mixtures, and thus the process shown in eq 1 seems indicated. That the extent of $Me_3Si$ cleavage exceeded the amount of trifluoroacetic acid originally charged no doubt is due to the presence of small concentrations of moisture which would serve to hydrolyze the $Me_3SiO_2CCF_3$, regenerating trifluoroacetic acid.



(1)



(2)

An experiment was carried out in which 1,2-bis(trimethylsilyl)benzene was heated in the presence of $CF_3CO_2H$ in benzene-$d_6$ solution. Examination of the reaction products by mass spectroscopy and nmr failed to give any evidence of incorporation of deuterium. Thus any involvement of solvent in the isomerization process seems ruled out.

Further information concerning the nature of this isomerization reaction was sought by heating an equimolar mixture of 1,2-bis(trimethylsilyl)benzene and 1,2-bis(triethylsilyl)benzene in the presence of a catalytic quantity of trifluoroacetic acid at 152° for 48 hr. When 1.3 mol % of catalyst was used, each compound rearranged to an extent of approximately 50% to the respective 1,3 isomer. Only traces of the cross-over product, 1-trimethylsilyl-2-triethylsilylbenzene, were observed. When 3.0 mol % of trifluoroacetic acid was employed as catalyst, rearrangement to the respective 1,3-disilylbenzene was complete for both 1,2-disilylbenzene starting compounds. In addition, the cross-over product was formed in *ca.* 10% yield. Since the amount of cross-over product was not that expected from a random distribution of $Me_3Si$ and $Et_3Si$ groups, we conclude that the major 1,2 → 1,3 isomerization is not an intermolecular one. The small amount of the scrambled product formed may have arisen in an independent redistribution reaction, of the type known to occur in organosilicon systems in the presence of Lewis acids such as aluminum bromide.[2]

Acid-catalyzed isomerizations of 1,2-diisopropylbenzene[3] and 1,2-diethylbenzene[4] *via* 1,2-alkyl shifts have been described by Olah, and the mechanism for the acid-catalyzed rearrangement of 1,2-bis(trimethylsilyl)benzene to its 1,3 and 1,4 isomers that best explains all of our observations is one analogous to that

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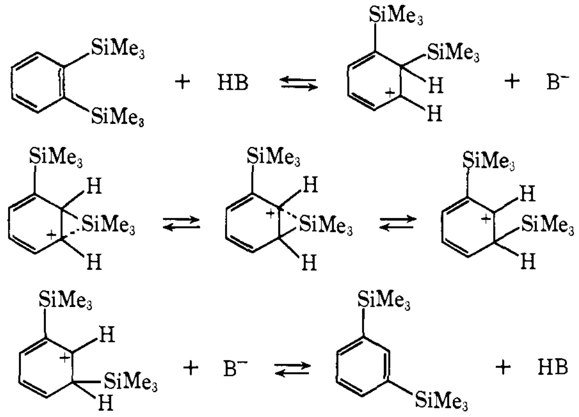
(2) G. A. Russell, *J. Amer. Chem. Soc.*, **81**, 4823 (1959).

(3) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2313 (1964).

(4) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *ibid.*, **29**, 2315 (1964).

proposed by Olah, *et al.*, for the isomerizations of the dialkylbenzenes mentioned (Chart I). That the acid is somehow involved in the rate-determining step was indicated by the fact that the rate of isomerization was dependent on the concentration of acid used. Proton transfer to carbon is probably the rate-determining step, since there is precedent for this in the desilylation of aromatic silicon compounds by protonic acids.[5] Steric repulsion between vicinal trimethylsilyl substituents seems to be the driving force in the isomerization. The 1,2 isomer rearranged to the 1,3 isomer, which in turn rearranged only slowly to the 1,4 isomer. The 1,4 isomer rearranged relatively slowly to the 1,3 isomer. The relative initial rate of isomerization of 1,2-bis(trimethylsilyl)benzene is approximately 200 times faster than that of the 1,3 or 1,4 isomers. In the cases of the latter, the rate of isomerization is so slow that the acid catalyst was consumed by the competing desilylation reaction before thermodynamic equilibrium could be reached. 1,2-Bis(trimethylsilyl)benzene has a high reactivity with respect to desilylation by sulfuric acid–acetic acid, and this was attributed to steric acceleration.[6] However, the accelerating effect of steric factors associated with vicinal $Me_3Si$ groups on 1,2 shifts appears to be even greater and thus isomerization apparently proceeds toward thermodynamic equilibrium.

**Chart I.** Mechanism of the Acid-Catalyzed Rearrangement of 1,2-Bis(trimethylsilyl)benzene



The mechanism in Chart I accounts quite satisfactorily for the following observations: (1) that there is a preponderance of 1,3 isomer, (2) that the trimethylsilyl group is not detached completely from the aromatic ring during the isomerization, and (3) that the rearrangement is an intramolecular process.

It was of interest to examine the effect of catalytic amounts of trifluoroacetic acid under these general reaction conditions on other vicinally disubstituted benzenes containing group IV element substituents, in particular those for which nonbonded interactions would be less severe. Replacing methyl substituents of $Me_3Si$ groups with hydrogens should decrease the steric effects of the silyl group, and for this reason 1-dimethylsilyl-2-trimethylsilylbenzene and 1,2-bis(dimethylsilyl)benzene were examined. Under conditions (2.3 mol % $CF_3CO_2H$ in benzene, 152°, 48 hr) where 1,2-bis(trimethylsilyl)benzene had been converted to a mixture of 94% 1,3-, 4.5% 1,4-, and 1.5% 1,2-bis(trimethylsilyl)benzene, these compounds also isomerized, but to a lesser extent. 1-Dimethylsilyl-2-trimethylsilylbenzene was isomerized to a mixture of 71% 1,2, 27% 1,3, and 1% 1,4 isomers. 1,2-Bis(dimethylsilyl)benzene was isomerized to the extent of 7% under these conditions, giving a mixture of 93% 1,2, 4% 1,3, and 3% 1,4 isomers. The explanation which comes immediately to mind when one considers this decreased tendency toward isomerization as $Me_3Si$ groups are replaced by $Me_2HSi$ groups is one in terms of decreased steric acceleration of rearrangement because of decreased nonbonded interactions between the vicinal substituents. However, another possible explanation must be considered, namely, that the acid catalyst is destroyed by reaction with the Si–H bonds present in the dimethylsilyl-substituted benzenes before significant isomerization can take place. (Acidolysis of organosilicon hydrides is a known reaction.[7]) If the latter explanation were to be the correct one, then one might expect that a compound such as 1,2-bis(dimethylsilyl)benzene would inhibit the acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene by consuming the acid present. This was not the case. In an experiment in which a solution containing approximately 0.2 mmol each of 1,2-bis(trimethylsilyl)benzene and 1,2-bis(dimethylsilyl)benzene and 0.005 mmol of trifluoroacetic acid in benzene was heated for 22 hr at 152°, the following isomer ratios were obtained: 1,2-bis(trimethylsilyl)benzene gave 97% 1,3 and 3% 1,4 isomer; 1,2-bis(dimethylsilyl)benzene gave 97% 1,2 and 3% 1,3 isomer. This is not a definitive experiment since the isomerization of 1,2-bis(trimethylsilyl)benzene could occur at a much faster rate than that of the reaction of Si–H bonds of 1,2-bis(dimethylsilyl)benzene with trifluoroacetic acid.

The effect of catalytic quantities of trifluoroacetic acid on 1,2-bis(trimethylgermyl)benzene and 1-trimethylsilyl-2-trimethylgermylbenzene also was investigated. Benzene solutions of these compounds containing 2.3 mol % of $CF_3CO_2H$ were heated at 152° for 48 hr. 1,2-Bis(trimethylgermyl)benzene isomerized hardly at all; after the heating period the composition of the disubstituted benzene mixture was 99% 1,2 and 1% 1,3 isomer. A small amount of cleavage occurred as well, since trimethylphenylgermane was present in less than 5% yield. Isomerization to the extent of 5% occurred in the case of 1-trimethylsilyl-2-trimethylgermylbenzene, giving a mixture composed of 95% 1,2-, 2% 1,3-, and 3% 1,4-substituted trimethylsilyltrimethylgermylbenzenes. A small (<5%) amount of cleavage also was observed, and it is noteworthy that the only monosubstituted benzene present was trimethylphenylsilane. This implies that Ge–C cleavage was the only such reaction which occurred. In the case of these germanium-substituted benzenes two explanations again are possible for the small extent of isomerization which occurred. The first again involves diminished nonbonded interactions, as expected,[8] when silicon atoms in 1,2-bis(trimethylsilyl)benzene are replaced successively by one and two germanium atoms,

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[5] C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements," Vol. I, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, p 409.

[6] C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Chem. Soc. B*, 15 (1969).

[7] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, Chapter 6.

[8] C. F. Shaw III and A. L. Allred, *Organometal. Chem. Rev., Sect. A*, 5, 95 (1970).

thus leading to processes where steric acceleration plays a less important role. The second explanation again involves the destruction of the acidic catalyst before a significant amount of isomerization to the 1,3 and 1,4 isomers can occur, in this case by reaction with Ge–C(aryl) bonds present. Cleavage of Ge–C(aryl) bonds by acid occurs at a faster rate than the cleavage of Si–C(aryl) bonds. Thus Eaborn and Pande found that the rate of Ge–C(aryl) cleavage in $Et_3GeC_6H_5$ by aqueous ethanolic perchloric acid is 36 times faster than that of C–Si(aryl) cleavage in $Et_3SiC_6H_5$.[9] Although our reactions were carried out under quite different conditions of medium and temperature, we would expect, other factors being equal, $k_{Ge-C} > k_{Si-C}$ for metal–carbon bond cleavage by trifluoroacetic acid in our reactions.

Final confirmation that it was the second explanation which was the correct one, *i.e.*, that the acidic catalyst was consumed in Ge–C cleavage at a rate faster than that of the isomerization processes, was provided by the finding that 1,2-bis(trimethylgermyl)benzene inhibited the $CF_3CO_2H$-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene. In an experiment in which equimolar quantities of 1,2-bis(trimethylsilyl)benzene and 1,2-bis(trimethylgermyl)benzene were heated in benzene at 152° for 48 hr in the presence of 4 mol % of trifluoroacetic acid (conditions which caused rapid and complete isomerization of 1,2-bis(trimethylsilyl)benzene in the absence of additives), essentially no isomerization of the starting organosilicon compound was observed. At best, traces of the 1,3 and 1,4 isomers were formed. Trimethylphenylgermane was formed, but no trimethylphenylsilane could be detected. A minor amount of isomerization of the 1,2-bis(trimethylgermyl)benzene occurred.

With a knowledge that acid-catalyzed rearrangements of 1,2-bis(trialkylsilyl)benzenes are possible, it is of interest to consider previous organosilicon literature for other examples of such reactions. Aromatic compounds and chlorosilicon hydrides react in the presence of a Lewis acid such as $BCl_3$, $BF_3$, or $B(OH)_3$ at 200–300° to give arylchlorosilanes. When monosubstituted benzenes are used, meta- and para-substituted products predominate and little or no ortho isomer is formed.[10] The high proportions of meta and low or zero proportions of ortho products are consistent with isomerization toward a thermodynamic equilibrium. Indeed, *p*-tolylmethyldichlorosilane has been shown to undergo 50% isomerization to the meta isomer within 4 hr in the presence of $BCl_3$ and a small amount of $HSiCl_3$ under conditions similar to those used for the condensations.[11] The mechanism of this isomerization was not investigated, and these rearrangements well could involve alkyl group rather than silyl group migration.

**Comments on the Preparation and Spectroscopic Characterization of Bis(trialkylmetal)benzene Compounds of the Group IV Elements.** The 1,2-, 1,3-, and 1,4-disubstituted compounds required for the present study and for the previous, related investigation[1] as authentic samples were prepared by standard organometallic reactions. Isomeric purity of the samples prepared was of much greater importance to us than maximum yields. For compounds of type $(R_3M)_2C_6H_4$, where the two $R_3M$ substituents are the same, either the preformed di-Grignard reagent (meta and para) or the *in situ* Barbier procedure[12] served satisfactorily. $Me_3SiC_6H_4Li$ reagents (meta and para) were used in the preparation of $Me_3SiC_6H_4MR_3$ compounds. The corresponding ortho isomers were prepared from trimethyl-*o*-chlorophenylsilane using either the Wurtz–Fittig procedure[13] or the Grignard *in situ* entrainment procedure.[14] The yields of ortho-substituted $(R_3M)_2C_6H_4$ and $Me_3SiC_6H_4MR_3$ compounds obtained in these condensation reactions were rather low, and the best route to compounds of this type may well be the Diels–Alder reaction of the appropriate substituted acetylenes, $R_3MC{\equiv}CMR_3$ and $Me_3SiC{\equiv}CMR_3$ with $\alpha$-pyrone.[1] The yields obtained with this procedure range from 50 to 75%, and the danger of acid-catalyzed isomerization of the product (*cf.* introductory section) can be obviated by the addition of a base such as triethylamine. The recent description of a method for the preparation of $\alpha$-pyrone on a 5-mol scale[15] makes this route more feasible.

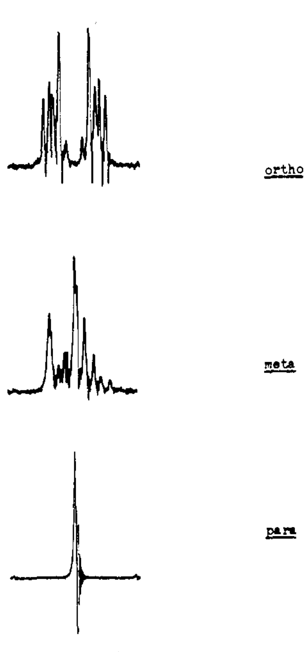

Figure 3. Nmr spectra of the aromatic protons of the isomeric bis(trimethylsilyl)benzenes.

The structural assignments of the isomers of the various group IV element disubstituted benzenes were confirmed by nmr spectroscopy. The nmr spectra in the aromatic region of a representative set of isomeric benzenes, 1,2-, 1,3-, and 1,4-bis(trimethylsilyl)benzene, are shown in Figure 3. The spectrum of the 1,2 isomer exhibits the symmetrical pattern of an aromatic AA′-BB′ system; that of the 1,3 isomer displays a distinctively unsymmetrical pattern. The aromatic protons of the 1,4 isomer appear as a sharp singlet. The nmr spectra of the other group IV element substituted ben-

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[9] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1566 (1960).

[10] Reference 5, pp 285–292.

[11] E. A. Chernyshev and E. V. Vagnits, *Zh. Obshch. Khim.*, 32, 24 (1962).

[12] R. G. Chaffee and H. N. Beck, *J. Chem. Eng. Data*, **8**, 453, 602 (1963).

[13] C. Eaborn, K. L. Jaura, and D. R. M. Walton, *J. Chem. Soc.*, 1198 (1964).

[14] D. E. Pearson, D. Cowan, and J. D. Becker, *J. Org. Chem.*, 24, 504 (1959).

[15] H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 2330 (1969).

zenes prepared were analogous to those of the isomeric bis(trimethylsilyl)benzenes. The effects of the group IV substituents apparently were quite similar, for the aromatic proton signals of all the 1,4 isomers prepared were singlets. Likewise, the nmr spectra of the various 1,2-disubstituted compounds exhibited a symmetrical AA'BB' or very nearly symmetrical ABCD patterns, similar to that of 1,2-bis(trimethylsilyl)benzene. The various 1,3 isomers prepared displayed distinctively unsymmetrical patterns in the aromatic region of the nmr spectra, quite similar to that of 1,3-bis(trimethylsilyl)-benzene.

The infrared spectra of the isomeric benzene compounds prepared were of lesser utility in isomeric structural assignment. Ultraviolet spectra also can serve to distinguish between 1,2, 1,3, and 1,4 isomers of disubstituted benzenes containing group IV element substituents, as we have shown in the case of 1,2-, 1,3-, and 1,4-bis(trimethylsilyl)benzene.[16]

## Experimental Section

**Trifluoroacetic Acid Catalyzed Rearrangement of 1,2-Bis(trimethylsilyl)benzene in Benzene Solution.** These reactions were carried out in bomb tubes, which were constructed from 16 × 125 mm Pyrex tubes that had been washed for 2 days in chromic acid solution, rinsed with water and acetone, and air-dried. The benzene solvent was Fisher reagent grade. Eastman trifluoroacetic acid was distilled (bp 72–72.5°) under nitrogen prior to use. The 1,2-bis(trimethylsilyl)benzene was purified by glc (20% UC-W98, 150°); 2.2232 g (9.993 mmol) was diluted to 5 ml with benzene to form a stock solution of substrate. Stock solutions of catalyst were similarly made from 0.0533 g (0.467 mmol), 0.1210 g (1.061 mmol), and 0.2265 g (1.986 mmol) of trifluoroacetic acid, each diluted to 10 ml with benzene. Expressed as mole per cent of substrate, the catalyst solutions were 2.3, 5.0, and 9.9%, respectively.

Each sample was prepared as follows: (1) 100 μl of substrate solution was carefully pipetted into the reaction tube, followed by 100 μl of benzene rinse; (2) 100 μl of the appropriate catalyst solution was carefully pipetted into the tube, followed by 100 μl of benzene rinse; (3) the tube was centrifuged to force droplets of solution that were clinging to the walls of the tube to the bottom; (4) the tube was connected to a vacuum manifold at 1 atmosphere *via* pressure tubing, and its contents were cooled in a liquid nitrogen bath; (5) the tube was partially evacuated (*ca.* 200 mm) to facilitate sealing and then was sealed. Solutions prepared in this manner had a total volume of 0.400 ml and were 0.500 *M* 1,2-bis-(trimethylsilyl)benzene and, depending upon the particular catalyst solution used, 0.012, 0.026, or 0.050 *M* trifluoroacetic acid.

After having been heated for the specified interval in a bomb-tube heater at 152 ± 2°, the tubes were removed and quickly cooled in a stream of cold tap water. They were then centrifuged in order to force to the bottom of the tube droplets that were clinging to its sides. The contents of the tubes were cooled in a liquid nitrogen bath, and the tubes were carefully cracked open using a white-hot Pyrex rod. They were capped tightly with 13-mm no-air stoppers while being allowed to warm to room temperature. The reaction mixtures, which were completely clear, colorless, and free from solids, were then examined by glpc (10% UC-W98). Several randomly selected samples were quantitatively analyzed under the above conditions using *p*-diethylbenzene as an internal standard. These products accounted for all of the silicon originally present, within experimental error. There were, however, exceptions to this at higher concentrations of catalyst (5%) and longer reaction times (7 and 10 days). In these cases, the above products contained a total of 0.34 ± 0.02 mmol of silicon, whereas 0.400 ± 0.004 mmol was originally present. There was, however, a small amount ($\leq 5\%$) of a component with the same retention time as that of trimethylsilyl trifluoroacetate in most of the samples, in addition to very small amounts (*ca.* 1%) of other lower boiling components. The number of these components and the large amount of solvent prevented isolation, identification, or accurate estimation of the quantity of these minor by-products.

The relative compositions of the samples were determined from the determined response factors and their glc peak areas. The results are tabulated in Tables I and II and are displayed graphically in Figures 1 and 2.

**Table I.** Rearrangement of *o*-Bis(trimethylsily)benzene Catalyzed by 2.3 Mol % of Trifluoroacetic Acid in Benzene at 152°

| Reaction time, hr | % yield PhSiMe$_3$ | % yield (Me$_3$Si)$_2$-C$_6$H$_4$ | Isomer distribution of (Me$_3$Si)$_2$C$_6$H$_4$ 1,2 | 1,3 | 1,4 |
|---|---|---|---|---|---|
| 3 | 2 | 98 | 76 | 22 | 2 |
| 6 | 6 | 94 | 54 | 43 | 3 |
| 12 | 8 | 92 | 44 | 53 | 3 |
| 25 | 12 | 88 | 12 | 83 | 5 |
| 48 | 13 | 87 | 1.5 | 94 | 4.5 |
| 96 | 14 | 86 | 0 | 93 | 7 |
| 169 | 16 | 84 | 0 | 92 | 8 |
| 240 | 18 | 82 | 0 | 92 | 8 |
| 240[a] | 0 | 100 | 99 | 1 | 0 |
| 240[b] | 0 | 100 | 100 | 0 | 0 |

[a] 5 mol % trifluoroacetic acid; room temperature. [b] 0.500 *M* in substrate with no trifluoroacetic acid.

**Table II.** Rearrangement of *o*-Bis(trimethylsilyl)benzene Catalyzed by 5.0 Mol % Trifluoroacetic Acid in Benzene at 152°

| Reaction time, hr | Normalized % yield PhSiMe$_3$ | Normalized % yield (Me$_3$Si)$_2$-C$_6$H$_4$ | Isomer distribution of (Me$_3$Si)$_2$C$_6$H$_4$ 1,2 | 1,3 | 1,4 |
|---|---|---|---|---|---|
| 3 | 8 | 92 | 53 | 44 | 3 |
| 6 | 10 | 90 | 36 | 60 | 4 |
| 12 | 15 | 85 | 9 | 84 | 7 |
| 25 | 17 | 83 | 0 | 92 | 8 |
| 48 | 18 | 82 | 0 | 92 | 8 |
| 96 | 23 | 77 | 0 | 89 | 11 |
| 169 | 32 | 68 | 0 | 84 | 16 |
| 240 | 32 | 68 | 0 | 85 | 15 |
| 240[a] | 0 | 100 | 99 | 1 | 0 |
| 240[b] | 0 | 100 | 100 | 0 | 0 |

[a] 5 mol % trifluoroacetic acid; room temperature. [b] 0.500 *M* in substrate without added catalyst.

The components of the reaction mixture were identified by comparison of their glc retention times and nmr and ir spectra with those of authentic samples.

This general procedure was used in all of the other trifluoroacetic acid catalyzed isomerization reactions carried out during the course of this study.

The data in Tables I and II are typical. Full details of all experiments mentioned in the Results and Discussion section can be found in the Ph.D. thesis of D. L. White (Massachusetts Institute of Technology, Aug 1970).

**Preparation of Disubstituted Benzenes Containing Group IV Element Substituents.** The following experiments are representative. Details concerning the products of these preparations are summarized in Table III.

**1,3-Bis(trimethylgermyl)benzene.** A 100-ml. three-necked flask equipped with a magnetic stirring assembly, a pressure-equalizing addition funnel, and a reflux condenser topped with an argon inlet was charged with 1.07 g (44 mg-atoms) of magnesium turnings and 25 ml of dry THF. To this mixture was added dropwise 5.20 g (22 mmol) of 1,3-dibromobenzene in 15 ml of THF. The reaction mixture was heated at reflux overnight to give a gray-white suspension. To the latter was added dropwise 6.12 g (40 mmol) of Me$_3$GeCl. The exothermic reaction which took place gave a clear, yellow solution. The reaction mixture was heated at reflux overnight, diluted with 25 ml of hexane, and hydrolyzed with saturated NH$_4$Cl solution. The dried organic layer was distilled to give 4.1 g (66%) of the desired product. An analytical sample was obtained by glc (20% UC-W98 on Chromosorb W, 175°).

**1,3-Bis(triethylsilyl)benzene.** A flask equipped as described above was charged with 1.34 g (55 mg-atoms) of magnesium

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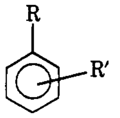
(16) D. Seyferth, D. R. Blank, and A. B. Evnin, *J. Amer. Chem. Soc.*, **89**, 4793 (1967).

Table III. Group IV Substituted Benzenes



| Isomer | R | R′ | Bp (mm) or mp, °C | $n^{25}$D | Lit. bp (mm) or mp, °C | Lit. $n^{25}$D | Ref | Analysis: found (calcd), % |  | Nmr, δ, ppm (in $CCl_4$) |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | Carbon | Hydrogen |  |
| 1,2 | $Me_3Ge$ | $Me_3Ge$ | 78.5–80.5 (0.55) | 1.5323 |  |  |  | 46.21<br>(46.27) | 7.22<br>(7.12) | 7.55–7.07 (m, 4), 0.42 (s, 18) |
| 1,3 | $Me_3Ge$ | $Me_3Ge$ | 73–75 (0.8) | 1.5085 |  |  |  | 46.07<br>(46.27) | 7.06<br>(7.12) | 7.47–7.22 (m, 4), 0.38 (s, 18) |
| 1,4 | $Me_3Ge$ | $Me_3Ge$ | 103–104 |  | 105–107 |  | *a* |  |  | 7.38 (s, 4), 0.37 (s, 18) |
| 1,2 | $Me_3Si$ | $Me_3Sn$ | 60–67 (0.03) | 1.5380 |  |  |  | 45.87<br>(46.03) | 7.07<br>(7.08) | 7.61–7.00 (m, 4), 0.30 (s, 9, with Sn satellites), 0.27 (s, 9) |
| 1,3 | $Me_3Si$ | $Me_3Sn$ | 68–70 (0.09) | 1.5170 |  |  |  | 46.15<br>(46.03) | 7.27<br>(7.08) | 7.57–7.17 (m, 4), 0.27 (s, 9, with Sn satellites), 0.23 (s, 9) |
| 1,4 | $Me_3Si$ | $Me_3Sn$ | 103–104 |  | 103–104 |  | *b* |  |  | 7.37 (s, 4), 0.27 (s, 9, with Sn satellites), 0.23 (s, 9) |
| 1,2 | $Me_3Si$ | $Me_3Ge$ | 76–78 (0.85) | 1.5222 |  |  |  | 53.68<br>(53.98) | 8.07<br>(8.31) | 7.70–7.10 (m, 4), 0.46 (s, 9), 0.33 (s, 9) |
| 1,3 | $Me_3Si$ | $Me_3Ge$ | 64 (0.75) | 1.4970 |  |  |  | 54.08<br>(53.98) | 8.39<br>(8.31) | 7.48–7.08 (m, 4), 0.37 (s, 9), 0.27 (s, 9) |
| 1,4 | $Me_3Si$ | $Me_3Ge$ | 98–98.5 |  | 98 |  | *c* |  |  | 7.37 (s, 4), 0.35 (s, 9), 0.23 (s, 9) |
| 1,2 | $Me_2HSi$ | $Me_2HSi$ | 65–68 (2.2) | 1.5113 | 129 (50) | 1.5101 | *d* |  |  | 7.63–7.13 (m, 4), 4.67 (sept, 2, *J* = 4 Hz), 0.33 (d, 12, *J* = 4 Hz) |
| 1,3 | $Me_2HSi$ | $Me_2HSi$ | 61–67 (2.4) | 1.4976 | 58–59 (1.1) | 1.4974 | *e* |  |  | 7.67–7.20 (m, 4), 4.43 (sept, 2, *J* = 4 Hz), 0.33 (d, 12, *J* = 4 Hz) |
| 1,4 | $Me_2HSi$ | $Me_2HSi$ | 67–70 (2.6) | 1.4999 | 94 (12) | $n^{20}$D 1.5005 | *f* |  |  | 7.52 (s, 4), 4.43 (sept, 2, *J* = 4 Hz), 0.33 (d, 12, *J* = 4 Hz) |
| 1,2 | $Me_3Si$ | $Me_2HSi$ | 75–76 (2.5) | 1.5069 |  |  |  | 63.58<br>(63.38) | 9.57<br>(9.67) | 7.55–7.17 (m, 4), 4.77 (sept, 1, *J* = 3.6 Hz), 0.35 (s, 9), 0.32 (d, 6, *J* = 3.6 Hz) |
| 1,3 | $Me_3Si$ | $Me_2HSi$ | 66–70 (2.25) | 1.4912 |  |  |  | 63.68<br>(63.38) | 9.63<br>(9.67) | 7.60–7.17 (m, 4), 4.40 (sept, 1, *J* = 4 Hz), 0.33 (d, 6, *J* = 4 Hz), 0.27 (s, 9) |
| 1,4 | $Me_3Si$ | $Me_2HSi$ | 76–76 (2.3) | 1.4942 |  |  |  | 63.69<br>(63.38) | 9.63<br>(9.67) | 7.37 (s, 4), 4.40 (sept, 1, *J* = 4 Hz), 0.33 (d, 6, *J* = 4 Hz), 0.27 (s, 9) |
| 1,2 | $Me_3Si$ | $Me_3Si$ | 80–82 (1.5) | 1.5125 | 89–90 (2.5) | 1.5111 | *g* |  |  | See Figure 3 |
| 1,3 | $Me_3Si$ | $Me_3Si$ |  |  | 112 (22) | 1.4867 | *h* |  |  |  |
|  |  |  |  |  |  | 1.4852 | *g* |  |  |  |
| 1,4 | $Me_3Si$ | $Me_3Si$ |  |  | 92–93 |  | *g* |  |  |  |
| 1,2 | $Me_3Si$ | $Et_3Si$ |  | 1.5048 |  |  |  | 68.36 (<br>(68.10) | 10.67<br>(10.67) | 7.62–7.15 (m, 4), 1.07–0.08 (m, 15), 0.25 (s, 9) |
| 1,3 | $Me_3Si$ | $Et_3Si$ | 77–79.5 (0.03) | 1.4938 |  |  |  | 68.38<br>(68.10) | 10.69<br>(10.67) | 7.67–7.25 (m, 4), 1.15–0.60 (m, $A_2B_3$, 15), 0.25 (s, 9) |
| 1,4 | $Me_3Si$ | $Et_3Si$ | 92 (0.03) | 1.4999 |  |  |  | 68.10<br>(68.10) | 10.64<br>(10.67) | 7.45 (s, 4), 1.15–0.60 (m, $A_2B_3$, 15), 0.25 (s, 9) |
| 1,2 | $Et_3Si$ | $Et_3Si$ |  | 1.5233 |  |  |  | 70.82<br>(70.50) | 11.13<br>(11.18) | 7.73–7.10 (m, 4), 0.68–0.39 (m, $A_2B_3$, 30) |
| 1,3 | $Et_3Si$ | $Et_3Si$ | 109–110 (0.03) | 1.4998 |  |  |  | 70.71<br>(70.50) | 11.08<br>(11.18) | 7.60–7.04 (m, 4), 1.27–0.47 (m, $A_2B_3$, 30) |
| 1,4 | $Et_3Si$ | $Et_3Si$ | 124–125 (0.03) | 1.5052 | 195–196 (16.5) |  | *i* | 70.73<br>(70.50) | 11.20<br>(11.18) | 7.37 (s, 4), 1.27–0.47 (m, $A_2B_3$, 30) |

[a] A. Leusink, J. G. Noltes, H. A. Budding, and G. J. M. Van der Kerk, *Recl. Trav. Chim. Pays-Bas*, **83**, 844 (1964). [b] O. Buchman, M. Grosjean, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **71**, 467 (1962). [c] V. F. Mironov and A. L. Kravchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1026 (1965). [d] Dow Corning Corp., British Patent 886,140 (1962); *Chem. Abstr.*, **57**, 2254 (1962). [e] Reference 12. [f] A. L. Klebanskii, L. P. Fomina, and S. B. Dolgoplosk, *Zh. Vses. Khim. Obshchest.*, **7**, 594 (1962); *Chem. Abstr.*, **58**, 4708 (1963). [g] Reference 16. [h] H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Amer. Chem. Soc.*, **73**, 3798 (1951). G. Grüttner and M. Cauer, *Ber.*, **51**, 1283 (1918).

turnings, 8.34 g (55 mmol) of $Et_3SiCl$, and 35 ml of dry THF. To this mixture was added, dropwise with stirring under argon, 5.85 g (25 mmol) of 1,3-dibromobenzene in 10 ml of THF. The reaction mixture was heated at reflux for 10 hr and then was worked up using the procedure described above.

**1-Trimethylsilyl-4-trimethylgermylbenzene.** A 500-ml, three-necked flask equipped with a mechanical stirrer, a pressure-equalizing addition funnel, an argon inlet tube, and a thermometer was cooled to −10° and charged with 15.0 g (65.5 mmol) of *p*-bromophenyltrimethylsilane and 75 ml of dry diethyl ether. *n*-Butyllithium in hexane (Foote Mineral Co.), 41 ml of 1.6 *M* solution, 65 mmol, was added dropwise. The reaction mixture was stirred at −10° for 30 min, and then 10.2 g (65 mmol) of trimethylchlorogermane in an equal volume of diethyl ether was added dropwise at a rate such that the temperature was kept at about −10°. The reaction mixture was stirred at room temperature overnight and heated at reflux for 1 hr. The mixture then was hydrolyzed with saturated ammonium chloride solution and the organic phase was evaporated at reduced pressure. The residual solid was recrystallized twice from hexane to give 12.9 g of the desired product, mp 96–98°.

**1-Trimethylsilyl-2-trimethylgermylbenzene.** A 200-ml, three-necked flask equipped with a mechanical stirrer, a pressure-equalizing addition funnel, and a reflux condenser topped with an argon inlet tube was charged with 3.0 g (130 mg-atoms) of sodium and 50 ml of dry toluene. The mixture was heated to reflux while being stirred vigorously. To the resulting molten sodium suspension was added dropwise a mixture of 9.4 g (51 mmol) of *o*-chlorophenyltrimethylsilane and 7.0 g (46 mmol) of trimethylchlorogermane. The reaction mixture was heated at reflux for 2 hr. While it was still warm, the mixture was filtered through a glass wool plug under nitrogen. The solid thus separated was washed with toluene. The combined filtrate and washings were hydrolyzed carefully with saturated $NH_4Cl$ and the organic phase was dried and distilled to give 4.2 g (33%) of the desired product. Glc examination of the distillate indicated 95% purity, and an analytical sample was obtained *via* glc (20% Carbowax 20M on Chromosorb P at 175°). (This yield is not typical; usually lower yields were obtained for compounds prepared by this procedure.)

**Acknowledgments.** The authors are grateful to the National Science Foundation for generous support of this work (NSF Grant GP 6466X) and to the IBM Corporation for the award of a fellowship to D. L. W. Gifts of chemicals by the Dow Corning Corp., Union Carbide Corp., M & T Chemicals, Inc., and the Eagle Picher Co. are gratefully acknowledged.

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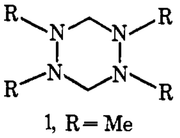
# Hexahydrotetrazine Conformations. The Effect of Substituents

**S. F. Nelsen* and P. J. Hintz**

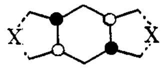
*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received August 26, 1971*

**Abstract:** The low-temperature nmr spectra of several symmetrically substituted tetraalkylhexahydrotetrazines are presented; at low temperatures both nitrogen inversion and (in most cases) ring flipping are slow on the nmr time scale. Substituents on the 1,2 and 4,5 nitrogens included $-(CH_2)_3-$; $-(CH_2)_4-$; $-CH_2CH{=}CHCH_2-$; Me,Me; and Et,Et. These compounds are shown to assume one of four different conformations at the hexahydrotetrazine ring, depending upon substituents. In only one case was more than one conformation observed by nmr; the Et,Et compound was (very approximately) an 85:15 mixture of two conformations at −90°. Significant differences in the chemical shifts observed for methylene groups attached to hydrazine and amino nitrogen are demonstrated, and very different anisotropic effects are shown to result from interaction with gauche and anti hydrazines.

The conformational analysis of hydrazines has been rather intensively studied since the realization that lone-pair interaction causes nitrogen inversion to be slow on the nmr time scale at accessible temperatures.[1] Although the conformations involved are sometimes clear, a controversy has arisen about the conformation of 1,2,4,5-tetramethylhexahydrotetrazine (**1**). Anderson and Roberts[2] found that both the methylene and methyl nmr singlets of **1** split up at low temperatures into an AB quartet and two singlets, respectively. Of the five fundamentally different conformations (**A–E**), three have the proper symmetry for the 1:1 methyl absorptions, but **1B** can be ruled out because of

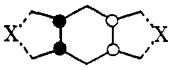


**1**, R = Me
**8**, R = Et

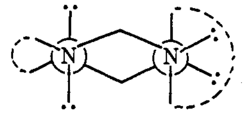


**A**

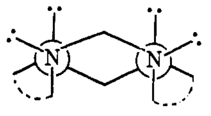
**B**



**C**



**A**



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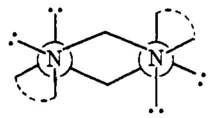

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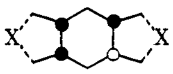
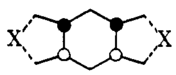
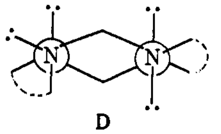
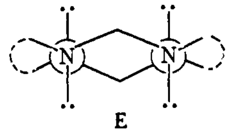






**D**



**E**

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(1) J. E. Anderson, *J. Amer. Chem. Soc.*, **91**, 6374 (1969), and references therein.

(2) J. E. Anderson and J. D. Roberts, *ibid.*, 90, 4186 (1968).