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SYNTHESIS OF 1,8-BIS(TRIMETHYLSILYL)- AND 1,8-BIS(TRIMETHYLSTANNYL)-NAPHTHALENE. THE RELATIVE STERIC EFFECTS OF CARBON, SILICON AND TIN IN THE 1,8-BIS(TRIMETHYLELEMENT)-NAPHTHALENES

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Summary

1,8-Bis(trimethylsilyl)- and 1,8-bis(trimethylstannyl)-naphthalene have been prepared by reaction of 1,8-dilithionaphthalene with trimethylchlorosilane and trimethyltin chloride. The steric effects of these Me_3M substituents in these compounds were evaluated by means of NMR spectroscopy. Acids and carbon tetrachloride were found to catalyze the rearrangement of 1,8-bis(trimethylsilyl)naphthalene to the 1,7-isomer.

Introduction

Steric strain associated with 1,8-disubstituted naphthalenes (*peri*-substitution) has received much attention [1]. Relief of such strain may be accomplished by: 1. in-plane deflection of the substituents; 2. out-of-plane deflection of the substituents; and 3. distortion or buckling of the aromatic nucleus itself.

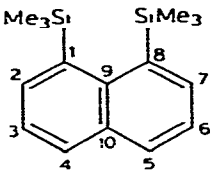
Recently, the synthesis of a series of 1,8-di-t-butylnaphthalenes has been reported [2]. It was estimated that incorporation of t-butyl groups in the *peri* positions would result in a strain energy of 37—38 kcal/mol. This strain later was shown to be partially relieved by an out-of-plane deflection of the t-butyl groups, which were found to be on opposite sides of the plane of the naphthalene ring [3]. As a consequence of this deflection, steric interactions of the t-butyl groups were reduced to such an extent that an unexpectedly low barrier to rotation of 6.5 kcal/mol was found.

The idea was expressed that steric interactions may occasionally produce low rather than high barriers to rotation [3]. As a change from a t-butyl group to a trimethylsilyl or trimethylstannyl group would change the steric requirements of the system, due to the differences in covalent radii of C, Si, and Sn, the

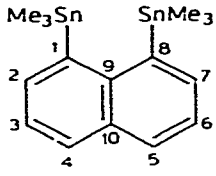
synthesis and NMR spectroscopic study of 1,8-bis(trimethylsilyl)naphthalene and 1,8-bis(trimethylstannyl)naphthalene was initiated.

Results and discussion

1,8-Bis(trimethylsilyl)naphthalene (I) and 1,8-bis(trimethylstannyl)naphthalene (II) were synthesized by treatment of 1,8-dilithionaphthalene [4] with tri-



(I)



(II)

methylchlorosilane and trimethyltin chloride, respectively. That I and II would exhibit different steric properties was suggested by the slow rate of formation of I as compared with the much faster formation of II under milder reaction conditions. It was found that a reaction time of 5 days in refluxing diethyl ether was required to obtain an 83% yield of I. In contrast, II was formed in 70% yield after 18 h at room temperature. Such unusually low reactivity of the Si–Cl bond toward a lithium reagent would indicate that the trimethylsilyl group experiences a greater steric influence in the *peri* positions than does the trimethylstannyl group.

This influence is clearly revealed in the ^{1}H NMR spectra of I and II. At room temperature, the spectrum of I shows singlets at δ —0.07, 0.24, and 0.53 ppm in a ratio of 3/1/2, respectively, attributable to the Si—CH_3 protons. If there were to be free rotation in I at room temperature, as in the 1,8-di-t-butylnaphthalene case [3], then the silicon-methyl resonances should appear as a singlet. The appearance of three signals, therefore, is interpreted in terms of hindered rotation about the silicon—naphthalene bonds. The same three resonances are found also at 150°C, indicating that there is a much higher barrier to rotation in I than in the t-butyl analogs. Considering this increased barrier to rotation, it would be logical to assume that the trimethylsilyl groups are deflected away from each other on opposite sides of the ring as in the t-butyl case [3]. However, unlike the t-butyl case where this deflection is sufficient to lower the barrier of rotation, the trimethylsilyl groups are locked in position.

It was surprising that the ^{1}H NMR spectrum of II at room temperature exhibited a singlet due to the trimethyltin groups. There was no evidence for any hindered rotation or line broadening as low as —100°C. A low barrier to rotation is indicated.

A possible explanation of these facts centers around the differences in covalent radii of C, Si, and Sn. Two competing factors are proposed to account for these observations. First, as the distance of a $(CH_3)_3M$ substituent from the naphthalene ring increases, the magnitude of the deflection of the substituent out of the aromatic plane also increases. This deflection would tend to lower the steric interaction of the *peri*-substituents. Second, as the covalent radius of the central atom of the substituent is increased, the distance of the methyl

groups from the center of the $(CH_3)_3M$ substituent also increases. This greater distance would tend to increase the steric interaction of the *peri*-substituents.

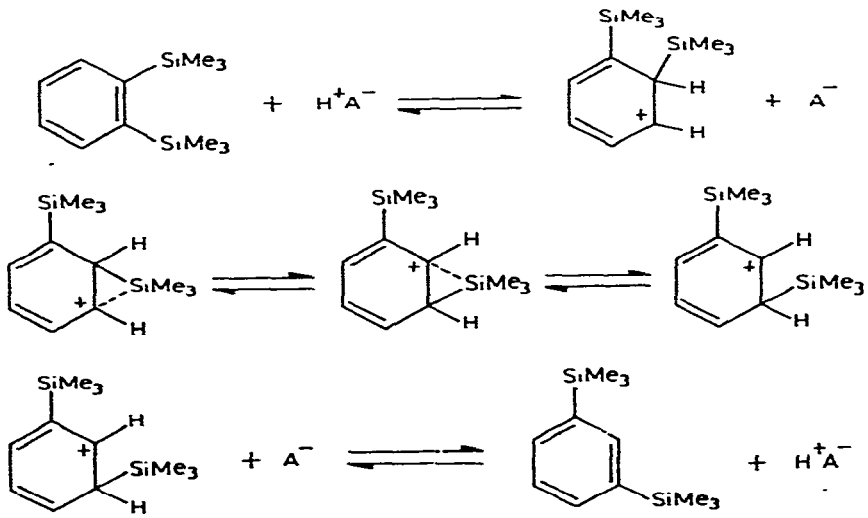
In the case of the 1,8-di-t-butylnaphthalenes, the deflection out of the aromatic plane is sufficient to overcome the steric interaction of the methyl groups. As a consequence, the methyl groups are able to slip past each other, and a low barrier to rotation is observed. In the case of I, the proposed larger deflection out of the plane is insufficient to overcome the steric interactions of the methyl groups, increased due to a longer Si—C bond, and a higher barrier to rotation is observed. In the case of II, the still larger deflection out of the plane is again sufficient to overcome the steric interaction of the methyl groups, even though the Sn—C bond is longer than the Si—C bond and presumably the interaction would, therefore, be larger.

It is interesting that the trimethyltin groups do not display as much steric hindrance as the smaller trimethylsilyl groups, but that the trimethylsilyl groups display greater steric hindrance than the t-butyl groups. It is clear then that steric hindrance does not depend solely on substituent size, but also on the relative geometry of the substituent and its relation to the molecule as a whole.

The trifluoroacetic acid-catalyzed rearrangements of 1,2-bis(trimethylsilyl)-benzene [5] and a series of 1,8-dimethylnaphthalenes [6] have been reported. In both cases, the primary rearrangement pathway involved a 1,2-migration of a substituent. The proposed pathway for the 1,2-bis(trimethylsilyl)-benzene rearrangement is shown in Scheme 1. The proposed pathway for the rearrangement of the 1,8-dimethylnaphthalenes was similar.

SCHEME 1

Mechanism of the acid-catalyzed rearrangement of 1,2-bis(trimethylsilyl)benzene [5]



The mechanism involves initial proton transfer from the acid to a substituted carbon on the aromatic ring. Subsequent rearrangement by a 1,2-migration and deprotonation give the products. Although both rearrangements were discussed in terms of a catalytic role of the acid, only in the 1,2-bis(trimethylsilyl)benzene

case was the acid used in catalytic quantities. In the case of the 1,8-dimethylnaphthalenes, reactions were carried out in refluxing trifluoroacetic acid as a solvent. In both cases, the driving force for the rearrangement was explained in terms of the relief of steric strain. That the ^{1}H NMR spectrum of 1,8-bis(trimethylsilyl)naphthalene exhibited hindered rotation about the silicon—naphthalene bond at temperatures up to at least 150°C indicates that a great deal of steric strain is incorporated into the molecule. It was felt, therefore, that treatment of 1,8-bis(trimethylsilyl)naphthalene under conditions where 1,2-bis(trimethylsilyl)benzene exhibits rearrangement would be worth investigating.

For this study, standard stock solutions of 1,8-bis(trimethylsilyl)naphthalene, trifluoroacetic acid, acetic acid, carbon tetrachloride, and triethylamine in dry benzene were used. Known amounts of the appropriate stock solutions were transferred by syringe to a nitrogen-purged NMR tube (medium walled). If required, the samples were diluted with dry benzene to insure the same concentration of 1,8-bis(trimethylsilyl)naphthalene in each tube. The contents of each tube are listed in Table 1. It should be noted that the catalytic species were present in approximately 2.5—3.0 mol % as compared with the naphthalene. The tubes were then sealed and placed in a Kugelrohr distillation oven thermostatted at 150°C (±1°C). The tubes were removed periodically, cooled in an ice—water bath, and an NMR spectrum of the silicon-methyl region of the contents was obtained. The tubes were then returned to the oven. As in the case of 1,2-bis(trimethylsilyl)benzene [5], isomerization was shown to be slow at room temperature, and it was assumed that the approximately 2—3 min periods at room temperature required to obtain the NMR spectra would not affect the isomerization rate significantly. Timing was halted while the tubes were at room temperature. Therefore, the measured time corresponds to the length of time each tube was at 150°C.

In all cases, except tube 7, the peaks due to 1,8-bis(trimethylsilyl)naphthalene diminished in intensity, while two new peaks grew in intensity. As was determined later, these two resonances correspond to the silicon-methyls of 1,7-bis(trimethylsilyl)naphthalene (see discussion below). Small amounts of some impurities (less than 5% of the silicon-methyls) were observed. Presumably, these result from cleavage of the trimethylsilyl—naphthalene bond as in the 1,2-bis(trimethylsilyl)benzene case [5]. As the amounts of such impurities were small,

TABLE 1

CONTENTS OF NMR TUBES FOR THE CATALYZED REARRANGEMENT STUDY [a]

Tube	Catalytic species (mmol)
1	—
2	CCl_4 (0.0052)
3	CF_3COOH (0.0063)
4	CF_3COOH (0.0063), CCl_4 (0.0052)
5	CH_3COOH (0.0060)
6	CH_3COOH (0.0060), CCl_4 (0.0052)
7	Et_3N (0.0052)
8	Et_3N (0.0052), CCl_4 (0.0052)

[a] Total volume in each case diluted to 420 μl with dry benzene if required. The amount of I used in each experiment was 0.206 mmol.

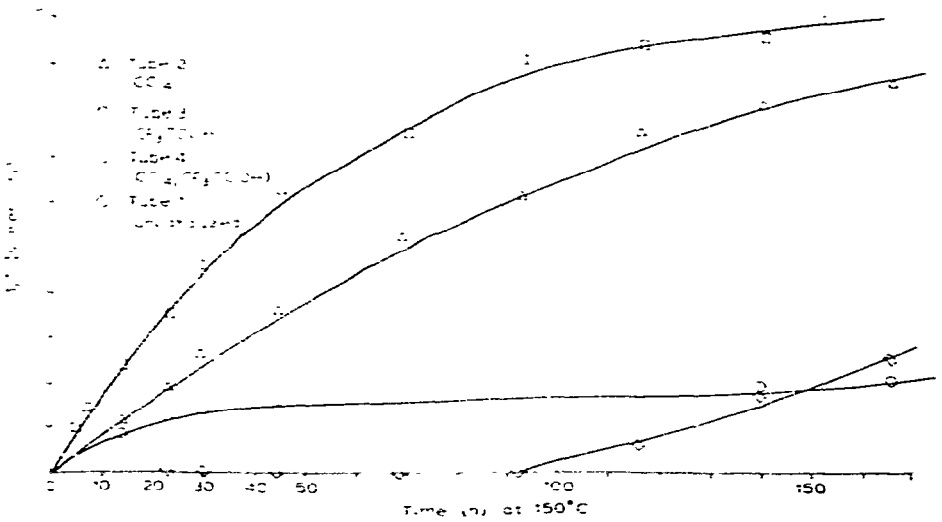


Fig. 1. Catalyzed isomerization of 1,8-bis(trimethylsilyl)naphthalene.

no attempt was made to identify or quantify them. The important numbers to be gained from this study were the 1,8- to 1,7-ratios. These ratios were obtained by measuring the peak heights of the δ −0.07 ppm resonance of the 1,8-isomer (with an intensity of 9H) and the δ 0.10 ppm resonance of the 1,7-isomer (also with an intensity of 9H). These heights then were related directly to the amounts of the corresponding isomers present at any one time. The results for each tube are presented in Fig. 1, 2 and 3 and in Tables 2, 1–8.

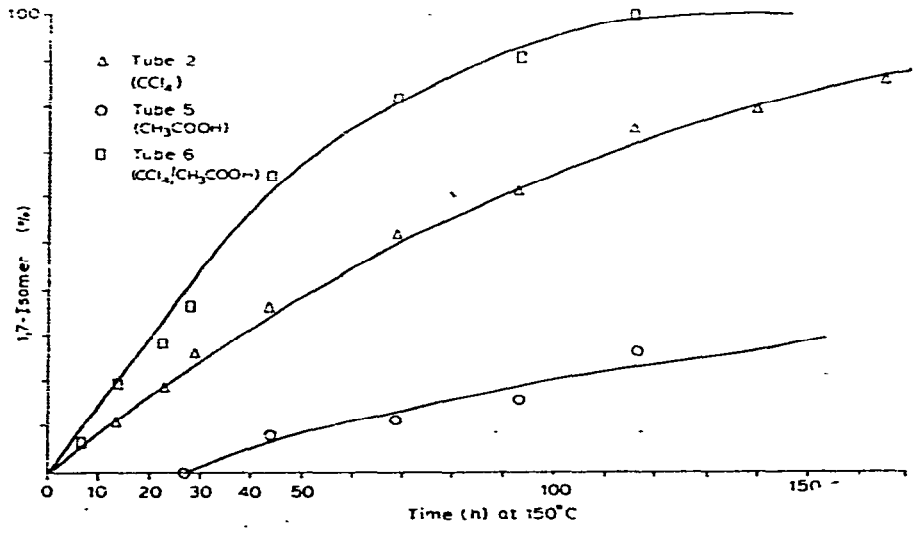


Fig. 2. Catalyzed isomerization of 1,8-bis(trimethylsilyl)naphthalene.

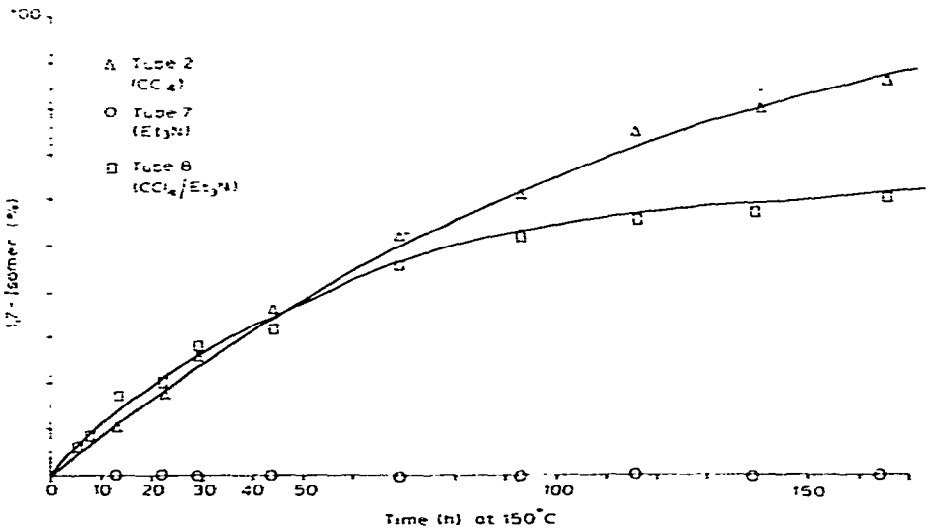


Fig. 3. Catalyzed isomerization of 1,8-bis(trimethylsilyl)naphthalene.

Several important facts may be noted. Isomerization was shown to occur slowly after 100 h at 150°C when no catalyst was added. This may be explained by the presence of some residual acid, which may have come from the glass NMR tube. In this regard, it must be mentioned that the NMR tubes (new) received no special pre-treatment other than washing with dry benzene and oven-drying. It was decided that any treatment might leave some unaccounted for residual acid or base which would adversely affect the results of these experiments.

The fact that triethylamine completely suppressed the isomerization displayed in the uncatalyzed reaction supported the idea that some residual acid was present in the case of the uncatalyzed reaction. The isomerization of 1,2-bis(trimethylsilyl)benzene [5] also was shown to be totally suppressed by addition of triethylamine.

The trifluoroacetic acid- (tube 3) and acetic acid-catalyzed (tube 5) reactions both were quite slow. With approximately 3 mol % of acid present, a reaction time of 100 h was required to achieve a 20% isomerization. Under similar conditions, the trifluoroacetic acid-catalyzed isomerization of 1,2-bis(trimethylsilyl)benzene was virtually complete after 60 h [5]. This slow rate of isomerization also may be explained by considering the steric hindrance of the two trimethylsilyl groups. If the trimethylsilyl groups are deflected out of and on either side of the plane of the aromatic nucleus, the naphthalene carbons at the 1 and 8 positions should experience a great deal of steric shielding. The trimethylsilyl group bound to C(8) would protect one side, while the other trimethylsilyl group would protect the backside of this carbon (see Fig. 4). This would hinder the approach of the protonating species, and as a result, the rate of isomerization would be slow. A similar shielding was postulated to ac-

(continued on p. 181)

TABLE 2

CATALYZED REARRANGEMENTS OF 1,8-BIS(TRIMETHYLSILYL)NAPHTHALENE

1. Uncatalyzed reaction:

Tube 1 contents:
300 μl of stock solution A (0.206 mmol of I)
120 μl of dry benzene.

Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
to 92.35	100	0
116.35	94	6
140.35	83	17
166.35	76	24
212.35	73	27

2. Carbon tetrachloride:

Tube 2 contents:
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution B (0.0052 mmol of CCl_4)
60 μl of dry benzene.

Time (h) at 150°C	1,8 Isomer (%)	1,7 Isomer (%)
to 7.08	100	0
14.17	92	8
23.58	82	18
28.88	74	26
44.88	64	36
68.88	48	52
92.88	39	61
116.88	25	75
140.88	19	81
166.88	14	86
212.88	12	88

3. Trifluoroacetic acid

Tube 3 contents
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution C (0.0063 mmol of CF_3COOH)
60 μl of dry benzene

Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
0.00	100	0
1.25	92	8
1.77	96	4
2.73	96	4
4.20	93	7
5.88	92	8
14.17	89	11
23.58	88	12
28.88	86	14
44.88	86	14
68.88	89	11
92.88	88	12
116.88	83	17
140.88	82	18
166.88	80	20
212.88	74	26

continued

TABLE 2 (continued)

4. Carbon tetrachloride and trifluoroacetic acid

Tube 4 contents
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution B (0.0052 mmol of CCl_4)
60 μl of stock solution C (0.0063 mmol of CF_3COOH)

Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
0.00	100	0
1.25	93	7
1.77	96	4
2.73	96	4
4.20	93	7
5.88	90	10
7.08	86	14
14.17	76	24
23.58	64	36
28.88	54	46
44.88	37	63
68.88	25	75
92.88	9	91
116.88	6	94
140.88	4	96
166.88	4	96
212.88	4	96

5. Acetic acid

Tube 5 contents
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution D (0.0060 mmol of CH_3COOH)
60 μl of dry benzene

Time (h) at 150°C	1,8-Isomer	1,7-Isomer
to 28.88	100	0
44.88	93	7
68.88	89	11
92.88	85	15
116.88	74	26
140.88	78	22
166.88	74	26
212.88	58	42

6. Carbon tetrachloride and acetic acid

Tube 6 contents
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution B (0.0052 mmol of CCl_4)
60 μl of stock solution D (0.0060 mmol of CH_3COOH).

Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
to 5.88	100	0
7.08	94	6
14.17	81	19
23.53	72	28
28.88	64	36
44.88	35	65

continued

TABLE 2 (continued)

Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
68.88	18	82
92.88	9	91
116.88	0	100
140.88	0	100
166.88	0	100
212.88	0	100

7. Triethylamine

Tube 7 contents
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution E (0.0052 mmol of Et_3N)
60 μl of dry benzene

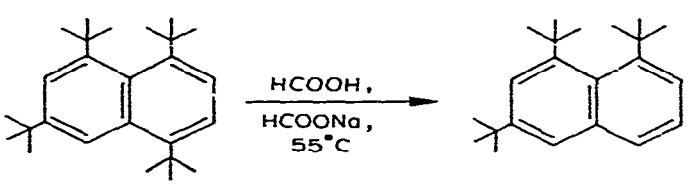
Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
to 212.88	100	0

8. Carbon tetrachloride and triethylamine

Tube 8 contents:
300 μl of stock solution A (0.206 mmol of I)
60 μl of stock solution B (0.0052 mmol of CCl_4)
60 μl of stock solution E (0.0052 mmol of Et_3N)

Time (h) at 150°C	1,8-Isomer (%)	1,7-Isomer (%)
4.20	100	0
5.88	94	6
7.08	92	8
14.17	83	17
23.58	81	19
28.88	72	28
44.88	68	32
68.88	64	36
92.88	58	42
116.88	54	46
140.88	53	47
166.88	50	50
212.88	44	56

count for the stability of *peri*-t-butyl groups toward acid-catalyzed dealkylation [2] (eq. 1).



(1)

The results from the carbon tetrachloride-catalyzed reactions (tubes 2, 4, 6, 8) were very interesting. Carbon tetrachloride appeared to be a better isomerization catalyst than either trifluoroacetic acid or acetic acid. The addition of triethyl-

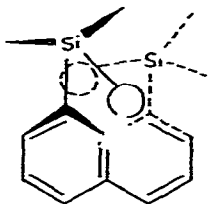


Fig. 4. Steric shielding of a *peri*-carbon by the trimethylsilyl groups in 1,8-bis(trimethylsilyl)naphthalene.

amine slightly retarded but did not completely suppress the rate of isomerization of I. Additionally, the presence of either trifluoroacetic acid or acetic acid increased the rate of isomerization of I.

Although these data do not allow a definitive statement to be made, it would appear that the effects of the carbon tetrachloride and trifluoroacetic acid (or acetic acid) are complementary. The evidence would seem to indicate that two reaction pathways are in operation for the isomerization of I. The acid-catalyzed pathway similar to that shown in Scheme 1 for 1,2-bis-(trimethylsilyl)benzene is slow due to the steric hindrance of the system. The other pathway, that promoted by the carbon tetrachloride, is much faster. This pathway does not appear to involve an acid-catalyzed rearrangement, as demonstrated by the fact that added triethylamine does not suppress completely the isomerization when carbon tetrachloride is present.

At this time, the reaction pathway involving carbon tetrachloride remains unknown, but a radical mechanism seems most probable in view of the well-known propensity of carbon tetrachloride to participate in radical processes.

The catalyzed rearrangements discussed above all gave rise to the same product as determined by NMR spectroscopy. In order to identify this product, a solution of 1,8-bis(trimethylsilyl)naphthalene and a catalytic amount (2.5 mol %) of carbon tetrachloride in a sealed NMR tube was heated at 150°C for 2 weeks. At the end of the heating period, the NMR spectrum revealed that the rearrangement had gone to completion. GLC analysis revealed the presence of only one product, which was collected and identified as a bis(trimethylsilyl)-naphthalene. Spectroscopic data for this compound may be found in the experimental section.

Initially, in the absence of confirming data from authentic samples of bis-(trimethylsilyl)naphthalenes, this compound was tentatively identified as 1,7-bis(trimethylsilyl)naphthalene on the basis of the following assumptions.

(1) Only one trimethylsilyl group would migrate. Once the steric grain associated with the substituents at the *peri* position is relieved, the driving force further rearrangements would be greatly reduced. This assumption is supported by the fact that only one product was produced in the isomerizations. No evidence for a second product was observed.

(2) The migrating group would not migrate to the second ring. It would seem that such a long distance migration would result in the production of more than one compound. This assumption rules out the 1,2-, 1,3-, and 1,4-isomers.

(3) The presence of two distinct trimethylsilyl resonances rules out a symmetrical molecule which would give only one silicon-methyl resonance. This

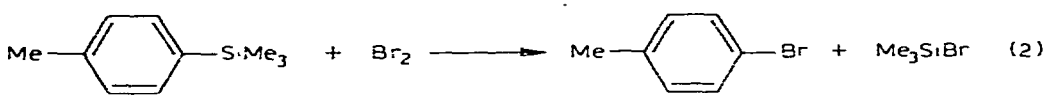
assumption rules out the 1,4- and 1,5-isomers.

(4) The migration is accomplished by a 1,2-shift of the substituent as in the case of 1,2-bis(trimethylsilyl)benzene [5] and the 1,8-dimethylnaphthalenes [6].

On the basis of the above assumptions, the product of the catalyzed rearrangements was identified as 1,7-bis(trimethylsilyl)naphthalene.

Evidence that the 1,7-isomer assignment was correct was obtained from the cleavage of the silicon—naphthalene bonds with bromine. Following the procedure of Eaborn [7], a solution of the rearrangement product in acetic acid (containing 1.5% of water by weight) was treated with bromine. After 30 min, GLC analysis revealed that only one product had been formed, which was identified as 2-bromonaphthalene. Rather than bromodesilylation, protodesilylation had occurred at the 1-position. As 1-trimethylsilylnaphthalene has been shown to protodesilylate much more rapidly than 2-trimethylsilylnaphthalene, because of steric acceleration at the *peri*-position [8], this result is not surprising.

Fortunately, a modification of Eaborn's method allowed successful bromodesilylations at both positions. When a benzene solution of the rearrangement product was treated first with bromine and then with acetic acid, GLC analysis revealed the presence of one major product which was identified as 1,7-dibromonaphthalene. As bromodesilylation of arylsilanes has been shown to result in regiospecific substitution of a bromine for the silyl group (e.g., eq. 2) [7], the



(2)

isolation of 1,7-dibromonaphthalene in this case is convincing evidence that the rearrangement product is 1,7-bis(trimethylsilyl)naphthalene. Analogous to the observed rearrangement of the 1,8- to 1,7-bis(trimethylsilyl)naphthalene, the acid-catalyzed rearrangement of 1,8-dibromonaphthalene has been shown to give only 1,7-dibromonaphthalene [9], thus further substantiating the assignment of the rearrangement product as the 1,7-isomer.

Experimental

General comments

All reactions were carried out under nitrogen using rigorously dried solvents. The standard reaction apparatus consisted of a three-necked, round-bottomed flask of suitable size equipped with a stirring unit (overhead or magnetic), a reflux condenser, a nitrogen inlet tube, and a pressure-equalizing addition funnel. Gas liquid chromatography (GLC) was used in determining yields and isolating pure samples for analysis and spectroscopy. A short (3.5 ft.) 20% SE-30 silicone rubber gum column, operated at 180°C, was used in this work.

Proton magnetic resonance spectra were obtained using a Varian Associates T60 or Perkin—Elmer R20 or R22 NMR spectrometers. Chemical shifts are reported in ppm downfield from internal tetramethylsilane.

Preparation of 1,8-dibromonaphthalene

1,8-Dibromonaphthalene was prepared by a modification of the literature

method for the preparation of this compound [10]. In a typical preparation, a five-liter, round-bottomed flask, equipped with an overhead stirring apparatus, an addition funnel, a low temperature thermometer, and a nitrogen inlet, was charged with 59.6 g (378 mmol) of 1,8-diaminonaphthalene (Aldrich) in one liter of 6.9 *M* sulfuric acid. The suspension was cooled to −20°C in a dry ice/acetone bath, and 80 g (1.15 mol) of sodium nitrite in 500 ml of water was added slowly. The temperature was maintained at −20°C throughout the addition. Immediately after the sodium nitrite solution was added, cuprous bromide (1.5 mol) in 500 ml of concentrated hydrobromic acid was added. The black solution was warmed carefully to 50°C. During the warming, a great deal of gas evolution was observed, causing a large quantity of foam to be produced which was very stable and threatened to push its way out of the flask. The addition of small quantities of diethyl ether was required to break up the foam. After 1 h, the solution was cooled to 10°C with the aid of an ice bath, and made alkaline to litmus paper by slow, careful addition of solid sodium hydroxide. The black residue was filtered and extracted with boiling THF until the extract was colorless (about one liter). The THF was removed from the filtrate by rotary evaporation to leave a red-black residue. This residue then was extracted with boiling diethyl ether until the extract was colorless (about one liter). (By using THF for the first extraction rather than diethyl ether, a smaller quantity of solvent was required for the extraction). The diethyl ether was removed from the filtrate by rotary evaporation to leave a dark red residue which was recrystallized from hexane to give 36.1 g of crude 1,8-dibromonaphthalene. The product was further purified by column chromatography (60 cm × 20 cm, silica gel, 10% benzene in hexane as eluent). Removal of the solvents by rotary evaporation gave 33.1 g (31% yield) of 1,8-dibromonaphthalene, m.p. 106—108°C (lit. [4] m.p. 106—108°C), the IR spectrum of which was identical with the published spectrum [4]. The yields of 1,8-dibromonaphthalene prepared in this manner typically are in the range 20—30%.

Reaction of 1,8-dilithionaphthalene with trimethylchlorosilane (reflux for 18 h)

The title dilithium reagent was prepared in the standard apparatus by treating a solution of 4.0 g (14.0 mmol) of 1,8-dibromonaphthalene in 100 ml of anhydrous diethyl ether with 14.0 ml (33 mmol) of 2.34 *N* n-butyllithium in hexane. An immediate exothermic reaction was noted. The mixture was stirred for 45 min, whereupon 4.5 ml (35.0 mmol) of trimethylchlorosilane was added. The mixture was heated at reflux for 18 h, allowed to cool to room temperature, and hydrolyzed with water. The organic layer was dried over magnesium sulfate. After filtration, volatile solvents were removed by rotary evaporation to leave a yellow, oily residue. GLC analysis revealed that two high boiling products had been formed. The first was collected (GLC) and identified as 1-trimethylsilylnaphthalene, n_D^{25} 1.5786 (lit. [11] n_D^{20} 1.5806), the NMR spectrum of which was identical with the published spectrum [11]. GLC yield determination showed the presence of 1.88 mmol (13%).

The second product (17% yield) was collected (GLC) and identified as 1,8-bis(trimethylsilyl)naphthalene, n_D^{25} 1.5567. NMR (CCl_4/CH_2Cl_2): δ −0.07 (s, 9H, $SiCH_3$), 0.24(s, 3H, $SiCH_3$), 0.53(s, 6H, $SiCH_3$), 7.19—8.08(complex, 6H, ring-H) ppm. Analysis: Found: C, 70.35; H, 9.00. $C_{16}H_{24}Si_2$ calcd.: C, 70.51; H, 8.88%.

Reaction of 1,8-dilithionaphthalene with trimethylchlorosilane (reflux for 120 h)

The title dilithium reagent was prepared in the standard apparatus by treating a solution of 4.80 g (16.8 mmol) of 1,8-dibromonaphthalene in 150 ml of anhydrous diethyl ether with 16 ml (35 mmol) of 2.2 *N* n-butyllithium in hexane. An immediate exothermic reaction was noted. The mixture was stirred for 45 min, whereupon 5.0 ml (40 mmol) of trimethylchlorosilane was added. The mixture was heated at reflux for 120 h, allowed to cool to room temperature, and hydrolyzed with water. The organic layer was dried over magnesium sulfate. After filtration, volatile solvents were removed by rotary evaporation to leave a yellow oily residue. GLC analysis revealed that one high boiling product had been formed. Distillation of the residue gave 3.82 g (83% yield) of 1,8-bis(trimethylsilyl)naphthalene as a clear, colorless liquid, b.p. 85—90°C/0.05 mmHg, the NMR and IR spectra of which were identical with those of authentic material.

Reaction of 1,8-dilithionaphthalene with trimethyltin chloride

The title dilithium reagent was prepared in the standard apparatus by treating a solution of 7.3 g (25.5 mmol) of 1,8-dibromonaphthalene in 150 ml of anhydrous diethyl ether with 23 ml (51 mmol) of 2.18 *N* n-butyllithium in hexane. An immediate exothermic reaction was noted. The mixture was stirred for 60 min, whereupon 10.2 g (51 mmol) of trimethyltin chloride in 40 ml of anhydrous diethyl ether was added; an exothermic reaction was noted. The mixture was stirred at room temperature for 18 h and was hydrolyzed with aqueous ammonium chloride. The organic layer was dried over magnesium sulfate. After filtration, volatile solvents were removed by rotary evaporation to leave a white solid residue. The solid was recrystallized from hexane to give 8.1 g (70% yield) of 1,8-bis(trimethylstannyl)naphthalene as white needles, m.p. 112.5—113.5°C.

NMR(CCl_4/CH_2Cl_2): δ 0.42(s, 18H, $J(^{117}Sn—H)$ 51 Hz, $J(^{119}Sn—H)$ 54 Hz, $SnCH_3$), 7.12—7.89(complex, 6H, ring-H) ppm. Analysis: Found: C, 42.37; H, 5.33. $C_{16}H_{24}Sn$ calcd.: C, 42.35; H, 5.33%.

Catalyzed rearrangements of 1,8-bis(trimethylsilyl)naphthalene (general procedure)

For these experiments, the following stock solutions were used: A. 0.686 *M* 1,8-bis(trimethylsilyl)naphthalene (I) in dry benzene; B. 0.086 *M* CCl_4 in dry benzene; C. 0.105 *M* CF_3COOH in dry benzene; D. 0.100 *M* CH_3COOH in dry benzene; and E. 0.087 *M* Et_3N in dry benzene.

The following general procedure (given here for tube 4, see Table 1) was used for the preparation of the samples. A new, medium walled NMR tube was oven dried and purged with nitrogen. Under a protective cover of nitrogen, 200 μl of solution A, 60 μl of solution B, and 60 μl of solution C were placed in the NMR tube. (All transfers were carried out by syringe techniques.) The tube was sealed in a flame and placed in a Kugelrohr oven thermostatted at 150°C (±1°C). The tube was removed periodically, cooled in an ice water bath, and an NMR spectrum of the silicon-methyl region of the contents was obtained. The ratio of the 1,8- to the 1,7-isomers present was determined by measuring the peak heights of the δ —0.07 ppm (from the 1,8-isomer) and the δ 0.10 ppm (from the 1,7-

isomer) resonances. The heights then were related directly to the amounts of the corresponding isomers present at any one time. The same method was used for preparing the other samples. The data from each experiment are shown in Table 2, 1–7.

Isolation and identification of the rearrangement product of 1,8-bis(trimethylsilyl)naphthalene

A dry, nitrogen-purged NMR tube was charged with 300 μl of stock solution A (0.206 mmol of I), 60 μl of stock solution B (0.0052 mmol of CCl_4), and 60 μl of dry benzene. The tube was sealed in a flame, and placed in an oven thermostatted at 150°C for 2 weeks. After this period of time, the NMR spectrum revealed the presence of only one compound (and a very small amount, less than 5%, of some minor impurities). GLC analysis also revealed the presence of only one compound, which was collected (GLC) and identified as 1,7-bis(trimethylsilyl)naphthalene, n_D^{25} 1.5527.

NMR (CCl_4/CH_2Cl_2): δ 0.10(s, 9H, $SiCH_3$), 0.52(s, 9H, $SiCH_3$), 7.10–8.02 (complex mult, 6H, ring-H) ppm. Analysis: Found: C, 71.04; H, 9.03. $C_{16}H_{24}Si_2$ calcd.: C, 70.51; H, 8.88%.

Treatment of the rearrangement product of 1,8-bis(trimethylsilyl)naphthalene with bromine in acetic acid

A dry, nitrogen-purged NMR tube was charged with 300 μl of stock solution A (0.206 mmol of I), 60 μl of stock solution B (0.0052 mmol of CCl_4), and 60 μl of dry benzene. The tube was sealed in a flame, and placed in an oven thermostatted at 150°C for 2 weeks. After this period of time, the NMR spectrum revealed the presence of only one compound (the rearrangement product of 1,8-bis-(trimethylsilyl)naphthalene. The tube was opened, and its contents were placed in a 25 ml round-bottomed flask, equipped with a stir-bar. The volatile solvents were removed by rotary evaporation. To the remaining oil was added 2.5 ml of glacial acetic acid and 40 μl of water (1.5% by weight of the acetic acid). The flask was capped with a no-air septum, and bromine (50 μl, 0.92 mmol) was added to the solution by syringe. A mildly exothermic reaction was noted. After 30 min, volatile solvents were removed by rotary evaporation to leave a yellow oil which was dissolved in 0.5 ml of benzene. GLC analysis of this solution revealed the presence of only one product which was collected (GLC) and identified as 2-bromonaphthalene, m.p. 58–59°C (lit. [12] m.p. 59°C), the NMR and IR spectra of which were identical with those of authentic material (Sadtler spectra nos. 546 and 14913, respectively).

In another experiment, a similar benzene solution of the rearrangement was treated first with 200 μl (3.66 mmol) of bromine. After 15 min, 150 μl of acetic acid was added to the solution. The mixture was allowed to stand at room temperature overnight, whereupon volatile solvents were removed by rotary evaporation. The remaining yellow oil was dissolved in 200 μl of benzene. GLC analysis of this solution revealed one major high boiling product, which was collected (GLC) and identified as 1,7-dibromonaphthalene, m.p. 73–74°C (lit. [9] m.p. 74.5–75.5°C). The IR spectrum of this compound revealed absorption bands at 620 and 599 cm^{-1}, characteristic of 1,7-dibromonaphthalene [9].

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References

1 For a review of early work see V. Balasubramanivan, Chem. Rev., 66 (1966) 567.
2 R.W. Franck and E.G. Lesser, J. Org. Chem., 35 (1970) 3932.
3 J.E. Anderson, R.W. Franck, and W.L. Mandella, J. Amer. Chem. Soc., 94 (1972) 4608.
4 R.L. Letsinger, J.A. Gilpin, and W.J. Vullo, J. Org. Chem., 27 (1962) 672.
5 D. Seyferth and D.L. White, J. Amer. Chem. Soc., 94 (1972) 3132.
6 A. Oku and Y. Yuzen, J. Org. Chem., 40 (1976) 3850.
7 C. Eaborn and D.E. Webster, J. Chem. Soc., (1957) 4449, and ref. therein.
8 C. Eaborn and D.E. Webster, J. Chem. Soc., (1959) 3034.
9 V.A. Koptyug, V.G. Shubin, and V.A. Plakhov, Zh. Obshch. Khim., 31 (1961) 4023.
10 H.H. Hodgson and J.S. Whitehurst, J. Chem. Soc., (1947) 80.
11 L. Birkofer and N. Ramadan, J. Organometal. Chem., 44 (1972) C41.
12 G. Harris (Ed.), Dictionary of Organic Compounds, 4th Edition, Vol. 1, Oxford University Press, 1965, p. 464.