

Preliminary communication

A new organosilicon rearrangement

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Examples of 1,2-shifts of alkyl substituents on aromatic rings have been well documented. Thus Olah and his coworkers have investigated the water-promoted AlCl_3 -catalyzed rearrangement of *o*-di-*t*-butylbenzene¹, *o*-*t*-butyltoluene², *o*-diisopropylbenzene³ and *o*-diethylbenzene⁴. To date similar rearrangement processes in benzenes containing two silyl substituents have not been reported. Indeed, in view of the facility with which various protonic acids and Lewis acids cleave the Si-C(aryl) bond⁵, observation of such acid-catalyzed rearrangements seemed only a remote possibility since it was quite possible that the acid catalyst would be consumed in such a cleavage reaction before rearrangement had occurred to a significant extent. Our experiments have shown that this is not the case.

When *o*-bis(trimethylsilyl)benzene was heated in benzene solution to 150° in the presence of 2.5 mole % of trifluoroacetic acid (sealed tube), its relative concentration fell exponentially to 2% within 48 h. At the same time, the concentration of the *meta* and *para* isomers rose to 93% and 5%, respectively, of the total bis(trimethylsilyl)benzenes present. There was little further change with time; the concentration of the *meta* isomer, having reached a maximum of 95% at ca. 72 h, fell slowly to 91% over the course of 240 h; the *para* isomer concentration rose slowly to 9% at 240 h. The results are presented in Fig. 1. Similar rearrangement carried out in the presence of 5 mole % of CF_3COOH occurred more rapidly, giving within 24 h a mixture containing 1% *ortho*, 91% *meta* and 7% *para* isomers (Fig. 2). In contrast *m*-bis(trimethylsilyl)benzene, when heated in benzene at 150° in the presence of 5 mole % of CF_3COOH , rearranged slowly to give, after 96 h, a mixture of 91% *meta* and 9% *para*-bis(trimethylsilyl)benzene. The *para* isomer also was rearranged under these conditions, a reaction at 150° in the presence of 3.8 mole % of CF_3COOH during 96 h giving a mixture of 93.5% *para* and 6.5% *meta* isomers. With 8.6 mole % of catalyst, a similar reaction for 96 h gave an 81/19 *para/meta* isomer mixture. In all of these reactions some of the protodetrimethylsilylation product, trimethylphenylsilane, was formed, the amount depending on the CF_3COOH concentration and the reaction time.

It should be emphasized that under these conditions (240 h at 152°), the individual bis(trimethylsilyl)benzene isomers are stable to rearrangement in the absence of an acidic catalyst.

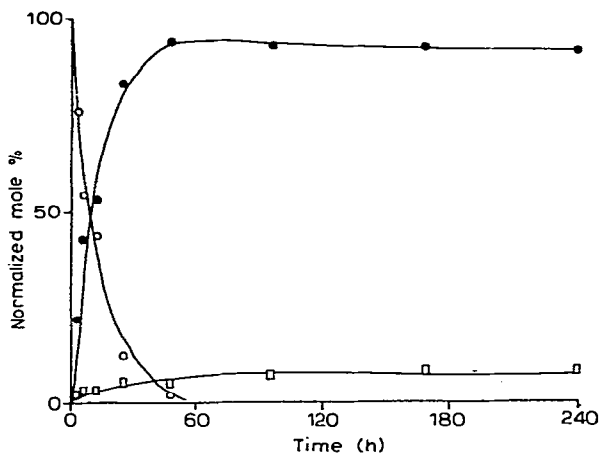


Fig. 1. Rearrangement of *o*-bis(trimethylsilyl)benzene catalyzed by 2.3 mole % of trifluoroacetic acid. \circ , *o*-(Me₃Si)₂C₆H₄; \bullet , *m*-(Me₃Si)₂C₆H₄; \square , *p*-(Me₃Si)₂C₆H₄.

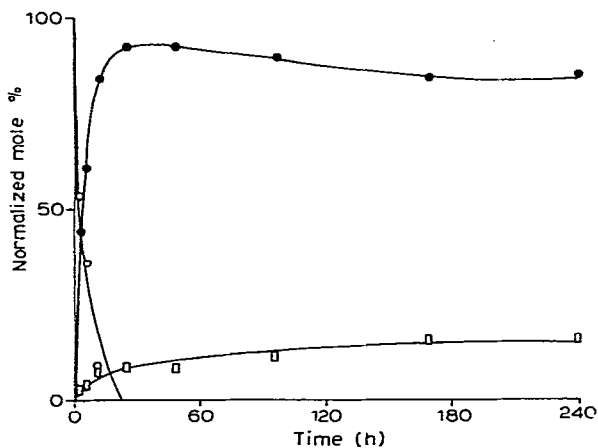


Fig. 2. Rearrangement of *o*-bis(trimethylsilyl)benzene catalyzed by 5.0 mole % of trifluoroacetic acid. \circ , *o*-(Me₃Si)₂C₆H₄; \bullet , *m*-(Me₃Si)₂C₆H₄; \square , *p*-(Me₃Si)₂C₆H₄.

o-Bis(trimethylsilyl)benzene also was rearranged in benzene-*d*₆ in order to determine whether or not the solvent was involved in any way in this reaction. No deuterium incorporation into either products or starting material was noted. A scrambling experiment was carried out in order to examine the possibility that the rearrangement was an intermolecular process. An equimolar mixture of *o*-bis(trimethylsilyl)benzene and *o*-bis(trimethylsilyl)benzene was heated at 150° for 48 h, in the presence of a catalytic amount of CF₃COOH. When the latter was present in 2.3 mole % concentration, each compound

rearranged to give approximately 50% of the respective *meta* isomer, and only traces of the scrambled product, *m*-Me₃SiC₆H₄SiEt₃, were observed.

The mechanism for these rearrangements that best explains all of our observations is one which is analogous to that proposed by Olah *et al.* for the acid-catalyzed rearrangements of *o*-diisopropyl- and *o*-diethylbenzene mentioned above (Chart I). That in our case the acid catalyst is involved in the rate-determining step is indicated by the observed

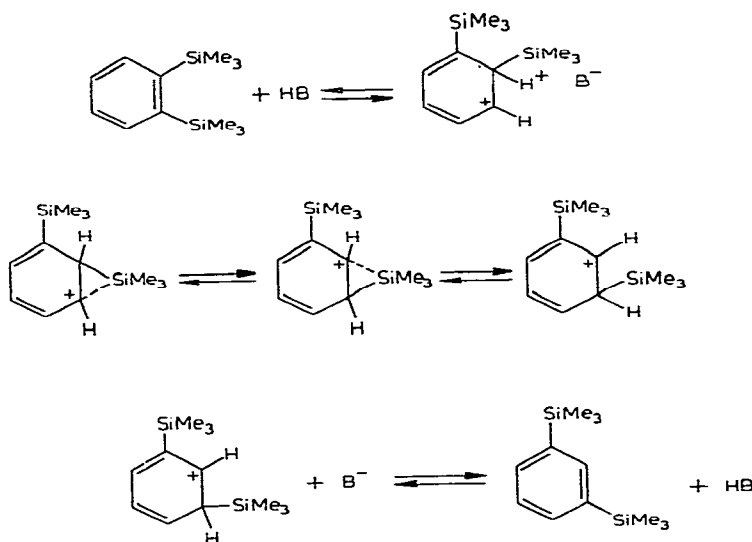


Chart I. Proposed mechanism of the acid-catalyzed rearrangement of *o*-bis(trimethylsilyl)benzene.

increase in rearrangement rate with increase in CF₃COOH concentration (Fig.1 and 2). Proton transfer to carbon probably is the rate-determining step, since there is precedent for this in the desilylation of aromatic silicon compounds by protonic acids⁵. It would seem that steric repulsion (*i.e.*, nonbonded interactions between Me₃Si groups attached to the same C₆ ring) is the driving force in this rearrangement★. The *ortho* isomer rearranged to the *meta* isomer, which then rearranged only relatively slowly to the *para* isomer, the steric repulsion having been largely eliminated. The *para* isomer rearranged relatively slowly to give only the *meta* isomer. The relative initial rate of rearrangement of *o*-bis(trimethylsilyl)-benzene is approximately 200 times that of the *meta* or *para* isomer. In the latter cases, the rate of rearrangement was so low that desilylation apparently destroyed the catalyst before thermodynamic equilibrium was reached.

The proposed mechanism accounts satisfactorily for the following observations: (1) the preponderance of *meta* isomer among the rearranged products; (2) that the tri-

★The high reactivity of *o*-bis(trimethylsilyl)benzene toward detrimethylsilylation by sulfuric acid/acetic acid has been attributed to steric causes⁶.

methylsilyl group is not detached completely from the aromatic ring during the rearrangement; and (3) that the rearrangement is intramolecular.

When similar experiments were carried out with *o*-bis(trimethylgermyl)benzene (heating at 150° in benzene for 48 h in the presence of 2 mole % CF₃COOH), it was found that practically no rearrangement occurred; the *meta* isomer was present but made up only 1% of the isomer mixture; a trace of the *para* isomer also appeared to be present. With the mixed compound *o*-Me₃SiC₆H₄SiGeMe₃ very similar results were obtained; the isomer mixture formed contained 95% *ortho*, 2% *meta* and 3% *para* isomers. These observations find an explanation in terms of the more ready protolysis of the Ge-C(aryl) bond as compared to the Si-C(aryl)⁷. The possibility mentioned in the introductory paragraph obtains in this case: the acid catalyst is consumed in Ge-C(aryl) bond protolysis at a faster rate than that of the rearrangement of the *ortho* isomer to the *meta*. In accord with this idea were the results obtained when an equimolar mixture of *o*-bis(trimethylsilyl)benzene and *o*-bis(trimethylgermyl)benzene was heated at 150° in benzene for 48 h in the presence of 2 mole % of CF₃COOH. Only trace quantities of *m*- and *p*-bis(trimethylsilyl)benzene were formed, and no trimethylphenylsilane. About 7% of the *o*-bis(trimethylgermyl)benzene had rearranged and some trimethylphenylgermane had been formed. It would appear that the presence of the *o*-bis(trimethylgermyl)benzene served to inhibit almost completely the rearrangement of *o*-bis(trimethylsilyl)benzene and that it did so by scavenging the acid catalyst initially present.

ACKNOWLEDGMENT

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