



Photochemical interconversions of benzenes and benzvalenes have been known for many years,<sup>8</sup> but we are specifically interested in thermal transformations. Isomerization of [5]metacyclophane to [5]orthocyclophane<sup>9</sup> and the skeletal scrambling of certain substituted pyridazines<sup>10</sup> may constitute examples of the process outlined in eq 1; however, these systems bear only a distant relationship to benzene itself. Ideally, the search for benzene automerization should be made using isotopic carbon labels. These are difficult to incorporate, however, so a preliminary study was conducted on a minimally labeled benzene using substituents held to carbon by strong bonds, i.e., fluorine atoms.

Isomerically pure  $C_6H_4F_2$  (Aldrich) was slowly evaporated (ca. 10 mg/h) into a stream of dry nitrogen which carried the sample through a hot, base-washed, quartz tube and then into a cold trap. Products were analyzed by GLC,  $^{19}F$ -NMR, and mass spectrometry. The starting material survived unchanged up to 1000°C; however, isomeric products began to appear as the temperature of the hot zone was raised still further (see Table).

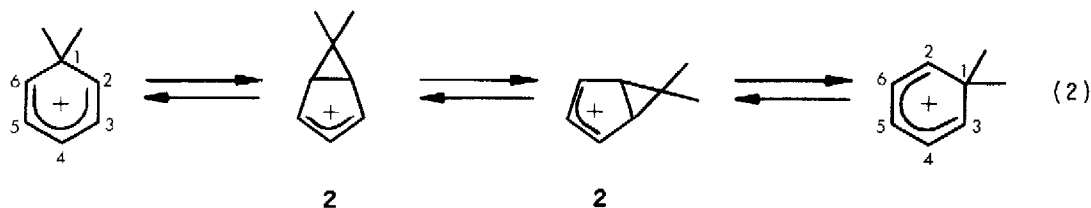
TABLE. Ratios of  $C_6H_4F_2$  isomers obtained from each isomerically pure  $C_6H_4F_2$  at 1096°C (contact time = 5 sec).

Starting Material \ Product	Product		
	ortho	meta	para
ortho	80	13	7
meta	5	81	14
para	4	18	78

Although these results are entirely consistent with the automerization mechanism depicted in eq 1, especially the more rapid accumulation of meta- $C_6H_4F_2$  when starting from either ortho- or para- $C_6H_4F_2$ , some complications seriously obscure the picture. At the high temperatures required to effect isomerization, less than 30% of the original  $C_6H_4F_2$  can be recovered as monomeric material after preparative GLC. In addition, the  $C_6H_4F_2$  isomers are accompanied by a substantial amount of  $C_6H_6F$  (33-42% of the monomeric material) and even a little  $C_6H_6$  (1.2-2.4%). Thus some rupture of C-F bonds clearly occurs.

It is possible, of course, that formation of  $C_6H_5F$  and  $C_6H_6$  could be completely unrelated to the observed automerization. Two pieces of evidence argue against the re-fluorination of  $C_6H_5F$  as a significant source of the  $C_6H_4F_2$  isomers reported in the Table: (1) Independent pyrolysis of  $C_6H_5F$  at 1096 and 1110°C gave considerable amounts of  $C_6H_6$  (19 and 32% of the monomeric material, respectively) but less than 0.1% of  $C_6H_4F_2$ . (2) In the pyrolysis of  $C_6H_4F_2$ , no more than 2.4% of  $C_6H_3F_3$  was ever obtained. Apparently, fluorine atoms can be lost but are not regained readily.

One plausible alternative to the benzvalene mechanism which could account for the observed isomerization of  $C_6H_4F_2$  is outlined below in eq 2. Thus, addition of a proton (from the wall?)<sup>11</sup> followed by disrotatory closure of the resulting pentadienyl cation<sup>12</sup> would give the bicyclic intermediate 2. Circumambulatory rearrangement of such cations has ample precedent,<sup>13</sup> and subsequent rearomatization<sup>12</sup> would lead to a benzene ring with carbon atoms 1 and 2 interchanged. If either carbon atom 1 or 2 were to bear a fluorine atom, isomerization would result. We have no evidence against this mechanism.<sup>14</sup>



The mechanism in eq 2 resembles a pathway proposed by Alder et al. for the gas phase isomerization of azulene to naphthalene.<sup>15</sup> Still other alternatives to the mechanistic proposals outlined in eqs 1 and 2 can also be envisaged to account for the results reported here.<sup>16</sup> Although it is possible that an intramolecular thermal automerization of the benzene ring may be responsible for the observed interconversions of ortho-, meta-, and para- $C_6H_4F_2$ , we cannot yet exclude the possibility of intermolecular mechanistic alternatives. Studies on benzene-<sup>13</sup>C<sub>2</sub> are underway.

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