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THE SYNTHESIS OF 1,2,5,6-DIBENZO-9-OXA-[3.3.1]-BICYCLONONA-2,6-DIENE, A NOVEL REACTION OF PHENYLACETALDEHYDE IN FLUOROSULFONIC ACID.

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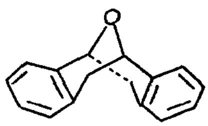
Since the behavior of organic molecules in strong acids is receiving considerable attention, we wish to report here a new reaction observed when phenylacetaldehyde (**1**) was treated with FSO_3H.

An ice-cold mixture of 2 g of **1** in 20 ml of CCl_4 and 8 ml of FSO_3H was stirred for 45 min at 0°C, poured over ice, and extracted successively with 550 ml of CCl_4 and 300 ml of ether. The extracts were washed with dilute $NaHCO_3$, combined, dried over $MgSO_4$, and concentrated under vacuum, yielding 1.09 g of residue, which was a single compound from NMR, and melted at 140-141° C after recrystallization from CCl_4-isopropyl ether.

This product resulted from the condensation of two molecules of **1**, since it had a molecular weight of 222 (mass spec.). It contained no carbonyl group, as indicated by its IR as well as C-13 NMR spectra. The IR showed a strong C-O band at 1070 cm^{-1}, and the C-13 NMR in $CDCl_3$ displayed two aliphatic carbons at 36.1 and 69.5, and six aromatic signals at 125.1, 125.9, 126.8, 129.1, 131.6, and 137.7 ppm. This small number of signals demanded that the molecule be quite symmetrical, a fact also apparent from the proton NMR spectrum, which showed aromatic signals at 6.7-7.1, in addition to only one methine at 5.13 and two methylene protons at 3.45 and 2.63 ppm, with a geminal coupling constant of 16 Hz, and vicinal constants of 0 and 6 Hz.

The structure of the product was unequivocally established by single crystal X-rays crystallographic analysis, and shown to be **2**.



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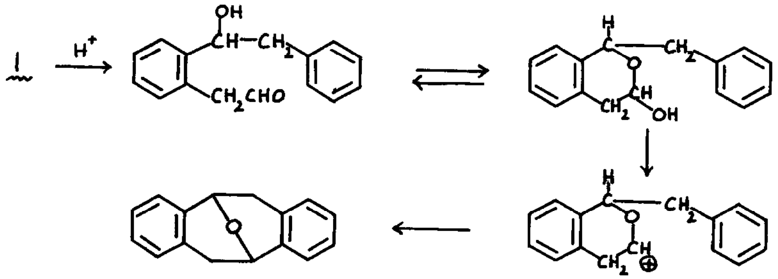
An attractive mechanism for the formation of **2** from **1** involves a double ortho aromatic substitution reaction, the second one utilizing the cation derived from the hemiacetal of the initially formed product.



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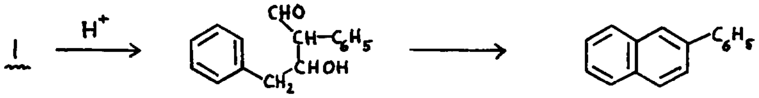
The isolation of 2 as the sole reaction product is noteworthy for three reasons:

a) The absence of aldol condensation reaction in an aldehyde where the alpha protons are also benzylic is unexpected. Previous treatments of 1 with other mineral acids[1,2] had yielded 2-phenylnaphthalene, and certainly involved an aldol condensation step, followed by cyclization and dehydration.[2,3]



b) The isomerization of the aldehyde into a ketone, a general phenomenon in strong acids,[4] was not observed here, and acetophenone was unreactive under the same conditions.

c) Although the parent 9-oxa-[3.3.1]-bicyclonona-2,6-diene itself has been prepared by three different methods,[5] there have been no reports to date on the synthesis of either its mono or its dibenzo analogs. Our procedure provides a particularly simple entry into the latter ring system, and can be extended to the synthesis of substituted derivatives.

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