

A DIRECT ENTRY TO A SEMIBULLVALENE STRUCTURE BY AN ABNORMAL DIELS-ALDER REACTION. MASS SPECTROMETRY EVIDENCE OF HIGHLY STABLE NON-BENZENOID AROMATIC CYCLOOCTATETRAENE DICATIONS.

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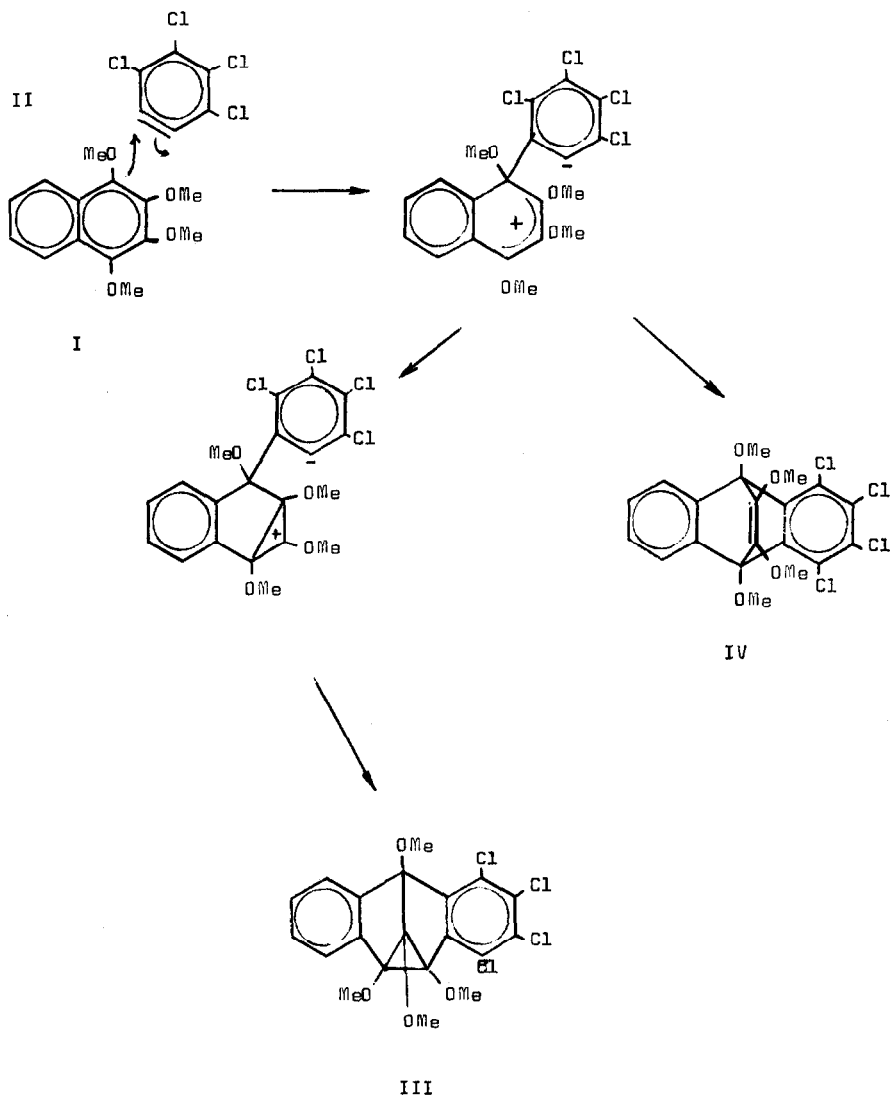
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Pursuing our studies on the synthesis of acetylene diethers via benzyne intermediates¹, we prepared 1,2,3,4-tetramethoxynaphthalene (I)⁺ (white crystals, m.p. 55-56°C; n.m.r. in DCCl_3 , τ 1.6-2.6 (m, AB system)(4H), 5.92 (s)(6H) and 5.95 (s)(6H); Found: C, 67.63; H, 6.41) which was then condensed with tetrachlorobenzene (II), generated in situ from hexachlorobenzene², and the reaction mixture chromatographed on alumina: two isomeric adducts were isolated in 7.5 and 1.3% yield, together with 35.8% of recovered tetramethoxynaphthalene I. The adducts were characterized, respectively, as the 1',2',3',4'-tetrachlorodibenzo-1,2,5,8-tetramethoxysemibullvalene (III)(m.p. 209-210°C; λ_{max} in cyclohexane, 216, 223 and 300 nm ($\epsilon = 71,900, 53,100$ and $1,602$); i.r. in KBr, no absorption in the region 2000-1500 cm^{-1} ; n.m.r. in DCCl_3 , τ 2.72-3.95 (m)(4H) and 6.0 (s)(12H); Found: C, 51.93; H, 3.56; Cl, 30.59) and 1',2',3',4'-tetrachlorodibenzo-1,2,3,4-tetramethoxybarrelene (IV)(m.p. 245-246°C; λ_{max} in cyclohexane, 227 and 276 nm ($\epsilon = 25,000$ and $2,450$); i.r. in KBr, 1675 and 1590 cm^{-1} ; n.m.r. in DCCl_3 , τ 2.4-2.95 (m)(4H), 6.04 (s)(6H) and 6.2 (s)(6H); Found: C, 51.92; H, 3.62; Cl, 30.78). These results are in contrast to those obtained from the reaction with 1,2-dimethoxynaphthalene¹ which gave only the normal 1,4-addition product in about 14% yield.

The formation of the semibullvalene derivative III can be rationalized assuming that the addition of tetrachlorobenzene to tetramethoxynaphthalene takes place in two stages

CHART I



-although not necessarily in two steps³-, as shown in Chart I, and probably it is the first reported example of a direct chemical entry to semibullvalene structures⁴.

In the other hand, in contrast also to the adduct from 1,2-dimethoxynaphthalene, which shows "normal" fragmentation in the Mass Spectrometer^{1,5}, compounds III and IV show a rather poor fragmentation, the base peak being at m/e 447 ($M^+ - 15$), i.e., only one methyl group is lost instead of any of the expected fragments: methoxy, methoxycarbyne or dimethoxyacetylene¹. However, the apparent anomaly is easily explainable if one realizes that cyclooctatetraene dications can be formed from the extremely electron-rich tetramethoxy species III and IV⁺⁺. The fragmentation for compound III is shown in Chart II. The relationship of barrelene structures, such as IV, with semibullvalene and cyclooctatetraene has been repeatedly noted⁴.

Whereas cyclooctatetraene dianion has been extensively studied either from the theoretical and the experimental points of view, and references to it are legion⁶, very little is known⁷ about the corresponding dication, which according to Hückel's rule ought to be a six π -electron aromatic species.

⁺ The synthesis of 1,2,3,4-tetramethoxynaphthalene will be reported with detail in the full paper.

⁺⁺ The referee's expectation that "if there is any substance in the Authors' hypothesis of stabilization of the $(M-15)^+$ ion by resonance participation of $(C_8H_8^{2+})$ -derived structures, then one would expect the parent M^{2+} ion to be present", is fully confirmed in the mass spectrum of the semibullvalene derivative III, which shows peaks at m/e 230, 231, 232 and 233 with the correct isotopic abundance due to the presence of four chlorine atoms.

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CHART II

