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ARYNE CHEMISTRY. PART XXIV.[1]

REACTIONS OF TETRAHALOGENOBENZYNES WITH BIPHENYLENE

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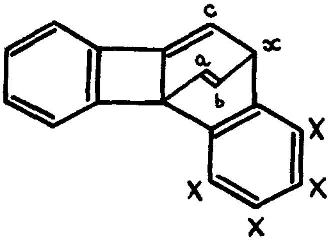
Biphenylene undergoes electrophilic substitution exclusively at the 2-position.[2] As far as we are aware no cycloaddition reactions of biphenylene have been reported. Thus although biphenylene and polymethoxybiphenylenes form charge-transfer complexes with for example maleic anhydride,[3] and tetracyanoethylene,[4] these do not collapse to cycloadducts. Benzyne, generated from o-fluorophenylmagnesium bromide,[5] or from 1-aminobenzotriazole,[6] does not react with biphenylene. Molecular orbital calculations[7] show the highest sum of the free valence index values for the 1,4-positions but the calculated product stabilities for the cycloaddition of maleic anhydride to biphenylene indicate that 2,4a-cycloaddition should be favoured.

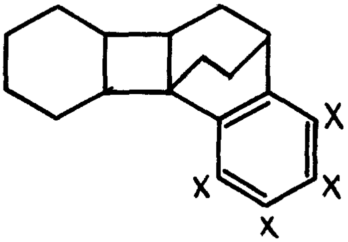
We have previously reported cycloaddition reactions of tetrahalogenobenzynes with a number of aromatic compounds in which high yields were obtained.[8] Reactions with naphthalenes always lead to cycloaddition at the 1,4-positions.

We now report that the decomposition of pentafluorophenyl-lithium in light petroleum in the presence of biphenylene (1 mole) led to the formation of a 1:1 adduct of tetrafluorobenzyne and biphenylene ($C_{18}H_8F_4$) in 12.5% yield. A very small amount of another product was also isolated and shown to be a 2:1 adduct ($C_{24}H_8F_8$) by mass spectrometry. Similarly the aprotic diazotisation of tetrachloroanthranilic acid in acetonitrile, in the presence of biphenylene (2 moles) gave an analogous 1:1 adduct of tetrachlorobenzyne and biphenylene in 6% yield.

Analysis and mass spectrometry established the molecular formulae indicated. The structures of the 1:1 adducts were evident from the following spectroscopic data for the chloro-compound (1a) (the spectra of the fluoro-compound were similar).



(1) a, X = Cl
b, X = F



(2) a, X = Cl
b, X = F

The ultraviolet spectrum showed $\lambda^{hexane}_{max.}$ 230 ($\log_{10}\epsilon$ 4.42), 248 (4.15), 270 (3.80), 281 (3.76), 294 (3.78),300 (3.77), and 308 (3.85) n.m., which, by comparison with the spectra for benzocyclobutene[9] and 1,2-dimethylenebenzocyclobutene,[10] indicates the presence of the methylenebenzocyclobutene chromophore. The ^{1}H n.m.r. spectrum showed resonances at τ 2.06 - 2.95 (4 aromatic protons), 3.1 (multiplet, protons a and b), 3.55 (doublet, $|J|$= 5.8 Hz., proton c), and 4.6 (multiplet, proton x). The mass spectrum shows the expected isotopic cluster for the presence of four chlorine atoms, and the major cleavage of the molecular ions occurs by the loss of chlorine and hydrogen chloride.

The reduction of (1a) with hydrogen in the presence of palladium on carbon resulted in the uptake of five moles with the formation of (2a). No definite break was observed in the uptake of hydrogen when the hydrogenation was interrupted after the addition of either one or two moles of hydrogen. The only product present was (2a) together with unchanged (1a). This result is in accord with the rapid reduction of benzocyclobutene by hydrogen in the presence of palladium.[11]

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