# Cycloaddition Reactions of [2,2](2,5)-Furanophane. Novel 1:1 and 2:1 Cycloadducts with Benzyne

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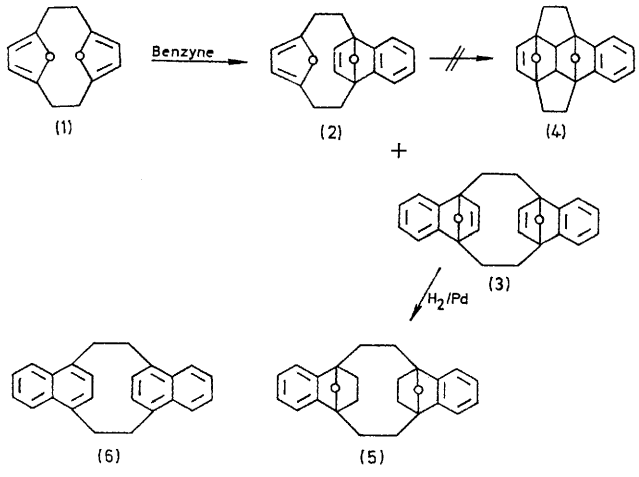
*Summary* Benzyne reacts with [2,2](2,5)-furanophane (**1**) to afford a non-internally cyclized 1:1 adduct (**2**) which on further reaction yields the first example, (**3**), of a 2:1 cycloadduct in this series.

IN the two previous examples of successful (4 + 2) cycloaddition to [2,2](2,5)-furanophane (**1**)[1] dienophiles dimethyl acetylenedicarboxylate[2] and tetrachlorocyclopropene[3] formed initial 1:1 cycloadducts that further cyclocondensed by means of a ready intramolecular (4 + 2) cycloaddition.[2,3] No trace of a 2:1 cycloadduct was detected even with a 2 mol. equiv. excess of either dienophile. Obviously for each of these dienophiles the second intermolecular cycloaddition is not competitive with internal cyclization.

In striking contrast to the above cycloadditions we report that reaction of furanophane (**1**) with benzyne affords a non-internally cyclized 1:1 adduct (**2**) which on further reaction with benzyne yields the first example, (**3**), of a 2:1 cycloadduct of this diene system.

Reaction of equimolar quantities of (**1**) and benzenediazonium-2-carboxylate hydrochloride in refluxing 1,2-dichloroethane[4] for 2 h followed by chromatography on silica gel afforded a 48% recovery of (**1**) in addition to 12·5% of the 1:1 adduct (**2**), m.p. 125—126° [$M^+$ (70 eV) 264; $\tau$ ($CDCl_3$) 3·17 (4H, AA'BB', ArH), 3·37 (2H, s, vinyl), 3·95 (2H, s, heterovinyl), 6·95—8·30 (8H, complex, $-CH_2-$)] and 13·3% of the 2:1 adduct (**3**), m.p. 224° (decomp.) [$M^+$ (70 eV) 340; $\tau$ ($CDCl_3$) 3·15 (8H, AA'BB', ArH), 3·43 (4H, s, vinyl), 7·47 (8H, AA'BB', $-CH_2-$)]. The presence of two vinyl-type signals in the n.m.r. spectrum of the 1:1 cycloadduct is clearly inconsistent with condensed structure (**4**). If formed (**4**) must readily cyclorevert as no evidence for its formation could be found.




Attempts to increase the yield of cycloadduction by employing two or more equivalents of benzyne precursor typically resulted in virtual disappearance of the monoadduct (**2**) with concomitant increase in the yield of bisadduct (**3**); however, total conversion was still in the 20—25% range. These results suggest that in competition for the reactive benzyne intermediate monodiene (**2**) is a considerably more efficient trapping agent than furanophane (**1**). The enhanced diene reactivity of (**2**) may be rationalized by an increase in internal strain and/or

electronic repulsions, but it is interesting that these same factors are insufficient to promote internal cycloaddition.

The stereochemical question as to whether the *syn* or *anti* isomer of bis-adduct (**3**) was produced in the benzene reaction is formally analogous to that previously resolved for [2,2]-paracyclonaphthane (**6**).[5] On the basis of the presumed *anti* structure for furanophane (**1**) and the favoured mode of benzyne approach during cycloadduction we favour the *anti* structure. Since in theory this structural problem could be resolved by transformation of (**3**) into one of the known isomers of (**6**) and in light of the simple acid-catalysed conversion of 1,2,3,4-tetrahydronaphthalene-1,4-*endo*-oxides into naphthalene derivatives,[6] bis-adduct (**3**) was catalytically hydrogenated to the tetrahydro adduct (**5**), m.p. *ca.* 290°; $M^+$ (70 eV) 344; $\tau$ ($CDCl_3$) 2·98 (8H, m, ArH), 7·68 (8H, m, $-CH_2-$), 8·38 (8H, m, $-CH_2-$). Unfortunately (**5**) proved to be unusually resistant to the bridge cleavage reaction in acidic media including concentrated sulphuric acid. Apparently the geometry in this system severely restricts formation of the requisite planar bridgehead cation.

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