Evidence for [2+2] and [4+2] Cycloadditions of Allylic Grignard Reagents to Benzyne

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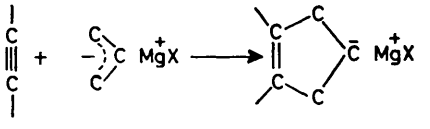
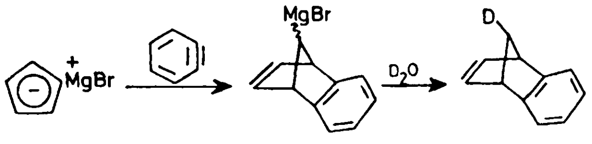
Summary In the presence of benzyne allylic Grignard reagents undergo three competitive reactions, *viz.* nucleophilic addition, concerted anionic 1,3-cycloaddition, and [2+2] cycloaddition.

BENZYNE undergoes nucleophilic addition as well as ($\pi^2 + \pi^2$) and ($\pi^4 + \pi^6$) cycloadditions and ene reactions.[1] We have studied the reactivity of benzyne with allylic Grignard reagents which would be expected to undergo all three types of reactions including the anionic 1,3-cycloaddition.[2] Anionic 1,3-cycloaddition can be achieved by a concerted process and therefore belongs to the ($\pi_s^4 + \pi_s^2$) type and is allowed by the Woodward–Hoffmann rules [equation (1)].[3]



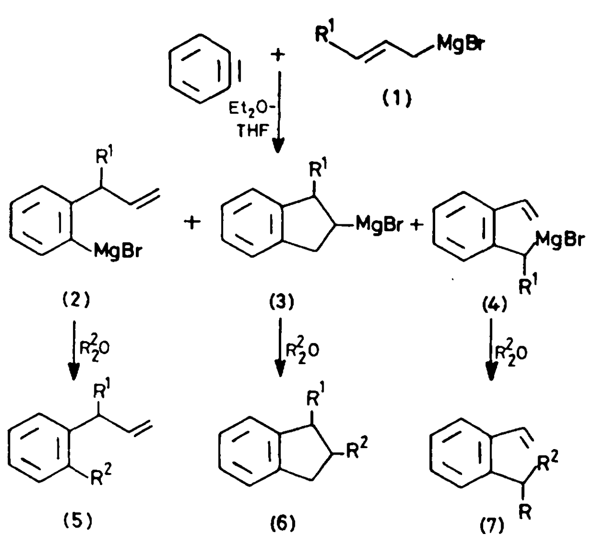
(1)

Ford *et al.*[4] have studied the reaction of cyclopentadienylmagnesium bromide with benzyne and the formation of the 9-norbornadienylmagnesium bromide may be explained in terms of either an anionic 1,3-cycloaddition or Diels–Alder cycloaddition (Scheme 1). They also reported[5] the cycloaddition of 2-phenylallylmagnesium phenoxide to *trans*-stilbene in the presence of crown ethers or hexamethylphosphoric triamide as catalysts, but the mechanism of this reaction was not studied.



SCHEME 1

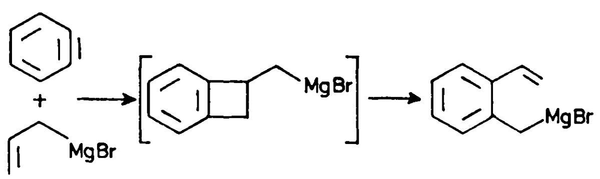
We now report that allylmagnesium bromide (**1**, $R^1 = H$) reacts with benzyne (prepared by the addition of *o*-bromofluorobenzene to magnesium) in ether–tetrahydrofuran (THF), to form a mixture of the three isomeric compounds [(**2**)—(**4**), $R^1 = H$] (Scheme 2).



Scheme 2. Relative yields: when $R^1 = H$, $R^2 = D$, (**5**) 65%, (**6**) 27%, (**7**) 8% [overall yield (**5**) + (**6**) + (**7**) = 30%]; when $R^1 = Me$, $R^2 = H$, (**5**) 57%, (**6**) 34%, (**7**) 9% [overall (**5**) + (**6**) + (**7**) = 50%].

Deuteriolysis of [(**2**)—(**4**), $R^1 = H$] gives [(**5**)—(**7**); $R^1 = H$, $R^2 = D$], respectively, with >98% of deuterium incorporation. Compound (**2**, $R^1 = H$) is formed by the nucleophilic addition of the Grignard reagent to benzyne.

A one-step anionic 1,3-cycloaddition presumably leads to (**3**, $R^1 = H$). Indeed (**2**, $R^1 = H$) does not cyclise to form (**3**, $R = H$); the ratios of [(**2**)—(**4**), $R^1 = H$] remain unchanged after heating the reaction mixture for a long period. We have synthesized, by the method described by Miller *et al.*,[6] the chloro-analogue of (**2**, $R^1 = H$) and confirmed his results: no change occurred after heating it in THF under reflux for 24 h. Product (**4**, $R^1 = H$) is formed by a $(\pi^2 + \pi^2)$ cycloaddition leading to a Grignard reagent which rearranges under the experimental conditions as shown by Hill (Scheme 3).[7]



Scheme 3

The reaction, of crotylmagnesium bromide (**1**, $R^1 = Me$) (Scheme 2) with benzyne gives [(**2**)—(**4**), $R^1 = Me$] which, on hydrolysis, afford [(**5**)—(**7**); $R^1 = Me$, $R^2 = H$]. The structures of compounds (**5**)—(**7**) have been established by n.m.r. and mass spectroscopy.

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