

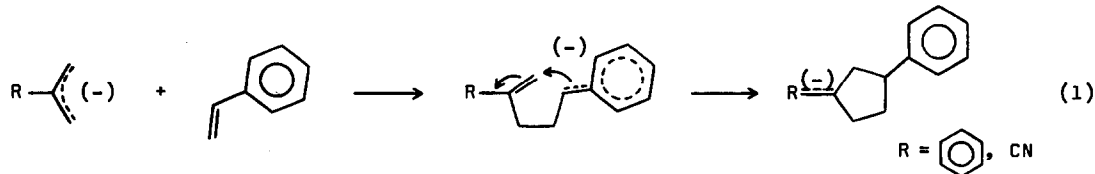
Novel cyclic products from intramolecular C=C addition of lithiated syn-7-norbornenyl allyl and benzyl ethers; Are 2+4 cycloadditions of allyl and benzyl anions with olefins concerted?

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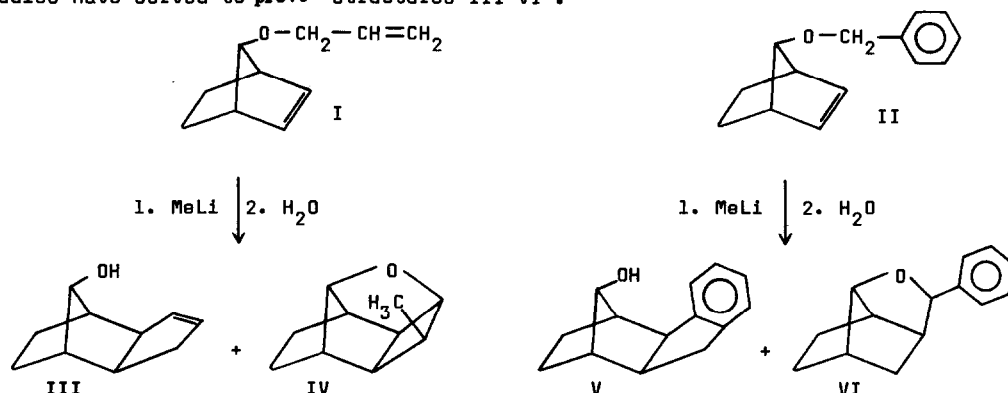
Cycloaddition of an allyl anion to a C=C double bond to form a cyclopentyl anion is seldom encountered. Only two reactions, involving phenyl ethylenes and allyl anions carrying phenyl or cyano at C-2 have been described<sup>1,2</sup>. These transformations could be  $\pi^2_s + \pi^4_s$  processes but their concertedness has not been proven<sup>3</sup>. Indeed their apparent substituent dependency is compatible with a two-step mechanism, both, phenyl and R stabilizing the intermediate, and R promoting the second addition step (eq. 1).



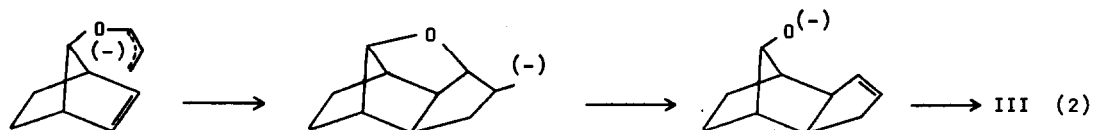
We wish to report on two cases of intramolecular allyl anion and benzyl anion induced cyclopentene formation, where phenyl groups at the double bond as well as substituents at C-2 of the allyl moiety are absent. As the olefinic reaction partner we chose the strained double bond of norbornene, which is very reactive towards 1,3-dipoles, the iso-electronic analogues of allyl anions<sup>4</sup>. An intramolecular source of allyl anions and benzyl anions was furnished by a syn-7-allyloxy or a syn-7-benzyloxy group. Allyl ethers are known to form upon metallation the more stable cis-alkoxy allyl anions needed for cycloaddition in our system<sup>5</sup>.

When ethers I and II were treated with excess methyl lithium in 1 : 1 ether : THF at room temperature no Wittig rearrangement ensued. Instead, after one hour with nearly all starting material consumed, hydrolysis yielded mixtures of compounds III and IV (3 : 7, 55%)

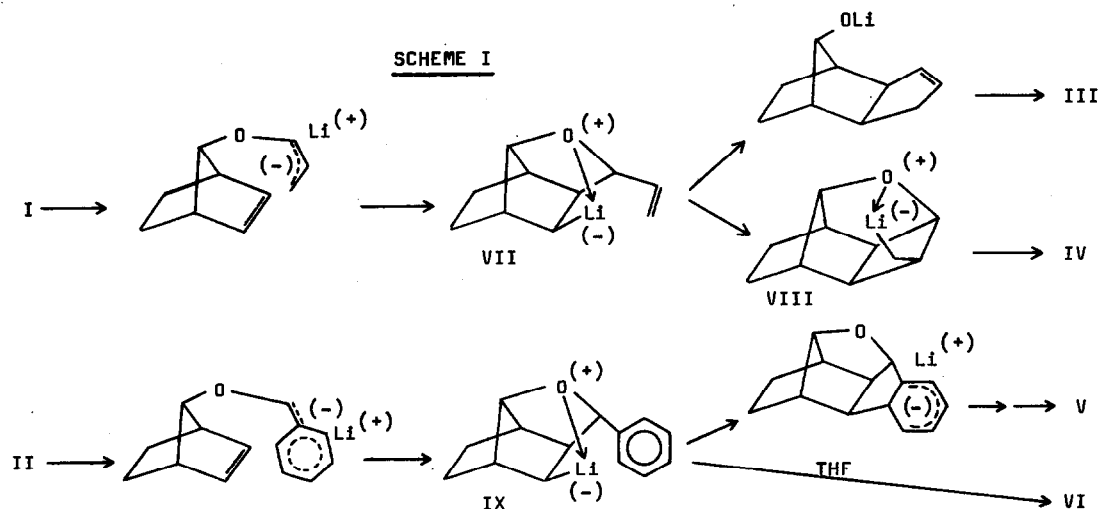
from I and V and VI (1 : 1, 52%) from II<sup>6</sup>. Spectral evidence, degradation, and synthetic studies have served to prove structures III-VI<sup>7</sup>.



Have III and V resulted from 2+4 cycloadditions followed by intramolecular elimination of alkoxide (cf. eq. 2) and - in the case of V - aromatization<sup>8</sup>?

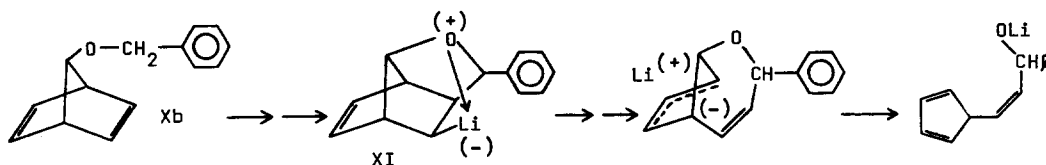


Considering that normally more ionic organolithiums are less reactive in additions to unconjugated C=C double bonds<sup>9</sup> the relatively high rates of (intramolecular) addition of ionic allyl and benzyl lithium in our cases seem to indicate the operation of novel factors, e.g. cyclic electron delocalization in transition states. Clearly, however, entropy factors, high reactivity of 1-alkoxyallyl and  $\alpha$ -alkoxybenzyl anions and intramolecu-



lar chelation (see structures VII, IX, and ref. 14) could as well have caused high rates of "normal" addition, leading to intermediates VII and IX from which III-VI could have originated via known processes<sup>10-12</sup> (see scheme I).

Support for the two-step mechanism comes from the reactions of 7-allyloxynorbornadiene (Xa) and 7-benzyloxynorbornadiene (Xb) with methyl lithium. Again starting materials were rapidly consumed, but dehydro-III and dehydro-V could not be isolated. Since the complex mixture of products formed from Xb reacted rapidly with maleic anhydride formation of cyclopentadienylic materials by intramolecular trapping of intermediate XI corresponding to IX is probable<sup>13</sup>.



A final decision as to the mechanism of formation of III and V must await results of further tests now underway.

Formation of the all-cis cyclobutane IV was surprising. D<sub>2</sub>O-quench of the reaction mixture of I lead to incorporation of deuterium into the methyl group of IV, therefore its immediate precursor must be VIII. Unlike its parent, cyclobutylmethyl lithium<sup>11</sup>, VIII does not rearrange to the ring-opened isomers VII and XII. More favorable intramolecular chelation in VIII must be responsible for this preference for VIII over its less strained isomers VII and XII<sup>14</sup>. An alternative mode of formation of VIII may be intramolecular charge-transfer controlled  $\pi_2s + \pi_2s$  cycloaddition as delineated by Epiotis<sup>15</sup>.



Extensions and variations of the intramolecular addition reactions described in this paper are under study.

#### Literature

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