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THERMAL REACTIONS OF ALLYLIC MONO- AND DIANIONS (1)

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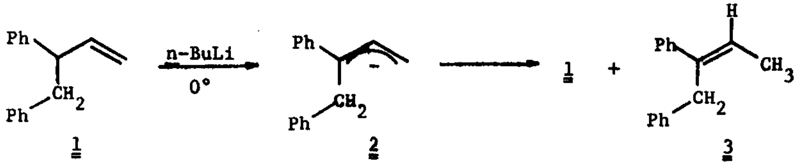
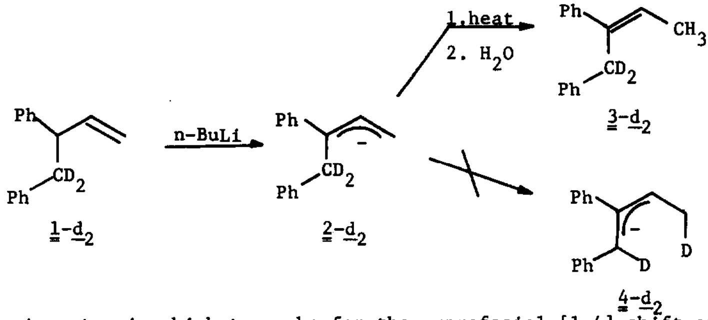
In the five years since its recognition, the principle of *conservation of orbital symmetry* (3) has found broad application not only towards the understanding and categorization of well-established "no-mechanism" reactions, but also in predicting new reactions and assigning characteristics to them. Despite the enormous success of the principle in the study of *neutral* systems, it would not be inaccurate to say that all of the work on *ionic* pericyclic reactions has just skimmed the surface of this interesting class of transformations. The only such systems whose scope, mechanism, and synthetic potential can be said to be thoroughly defined are the cationic allyl-cyclopropyl electrocyclic reaction (4), the cationic [1,2] sigmatropic shift (Wagner-Meerwein rearrangement), and the anionic [1,2] sigmatropic shift, especially of neutral ylides (5). We now report some preliminary results from our search for symmetry-allowed reactions of carbanions.

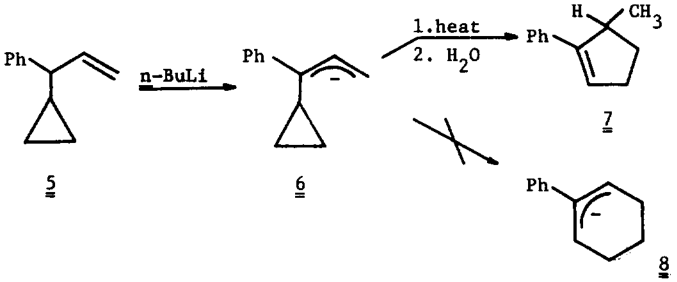
Because allylic organolithium reagents are generally considered to be delocalized ionic species (6), we felt that such reagents would be appropriate substrates at which to look for the thermally allowed suprafacial [1,4] sigmatropic shift of H (7). Reaction of 3,4-diphenyl-1-butene (**1**) at 0° with one equiv of *n*-butyllithium in 1:1 hexane/THF or hexane/TMEDA produces a deep-red solution containing allylic anion **2**. Water quench yields 17% of **1**, 78% of 1,2-diphenyl-*cis*-2-butene (**3**) (8), and 5% of uncharacterized material; nmr analysis of **3** from D_2O quench of **2** reveals the presence of better than 0.8 deuterium atom at C_4. When deuterium labeled **1**-d_2 is similarly treated with *n*-butyllithium in hexane/THF and the solution is refluxed overnight, quenching of the still deep-red solution yields **1**-d_2 and **3**-d_2 in nearly the same ratio as above. Analysis of **3**-d_2 provides no evidence of deuterium scrambling, thus ruling out any sigmatropic shift of the type **2**-d_2 → **4**-d_2. If one assumes that the formation of *cis* product **3**-d_2 establishes the geometry of **2**-d_2 as the *cis* allylic anion required for [1,4] shift, then the origin of the failure to observe such a reaction may be kinetic (difficulty in maintaining continuous overlap as the transition state is approached) or thermodynamic (non-bonded interactions of the phenyl

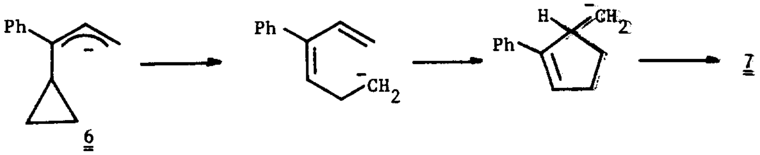


groups in 4-d_2).

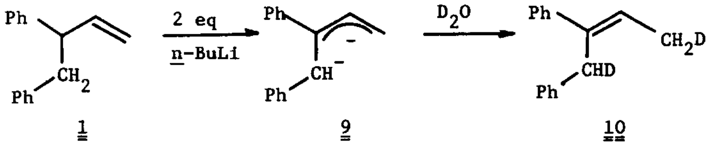


A system in which to probe for the suprafacial [1,4] shift of C (9) is anion 6 which has ring strain relief as additional driving force for rearrangement to 8. In fact, however, reaction of 5 with one equiv of n-butyllithium in hexane/TMEDA followed by heating at 60° for 1 hr produces cyclopentene 7 as the only characterizable product (43% yield). Although several possibilities exist, one plausible mechanism for the formation of 7 involves ring opening of cyclopropylcarbinyl anion 6 (10) followed by cyclization to a five- rather than a six-membered ring (11).

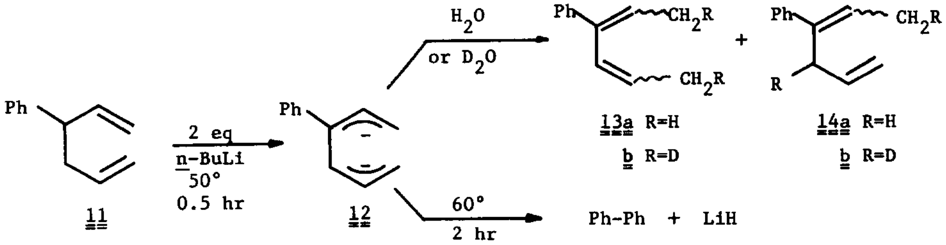




During the course of these studies, it became evident that systems like 1 were capable of consuming greater than one equiv of n-butyllithium and that the chemistry of the resulting anions was quite different from that discussed above. Thus, reaction of 1 with two equiv of n-butyllithium in hexane/TMEDA at 53° produces a dark red solution of dilithiated species 9 (12) which upon D_2O quenching produces dideuterated 10 (73% yield). 3-Phenyl-1-butene under these same conditions yields only the allylic monoanion; thus unsaturation at C_4 in 1 appears to be necessary for removal of the second proton (13).

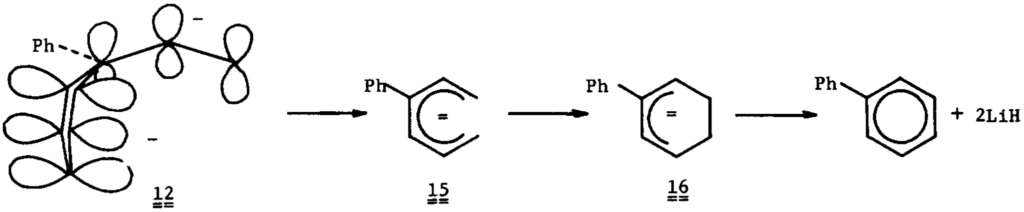


Similarly, diene 11 with two equiv of n-butyllithium at 50° leads to dianion 12 which upon quenching with H_2O produces 13a (36%) and 14a (17%) (stereochemistry unknown) and with D_2O produces dideuterated materials 13b and 14b. Heating a solution of 12 at 60°, however, yields



biphenyl as the only isolable product (77%); a light brown solid which collects on the walls of the flask and which reacts very vigorously with water is presumably LiH. Compound 11 with only one equiv of n-butyllithium under the same conditions affords only a trace of biphenyl.

A tempting rationalization for these results begins with the assumption that the allylic systems of 12 are orthogonal. Upon extended heating, rotation about C_3-C_4 occurs, producing



the planar 8π-electron delocalized dianion 15 which cyclizes (14) to 16. Loss of two moles of LiH (stepwise or concerted) would produce biphenyl; it is well-known that cyclohexadienyl monoanions readily lose LiH (15a), the formation of an aromatic ring apparently being responsible for the facile elimination as compared to other organolithium reagents (15b,c).

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