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ADDITION AND METALATION REACTIONS OF SMALL RING OLEFINIC HYDROCARBONS WITH BUTYLLITHIUM.

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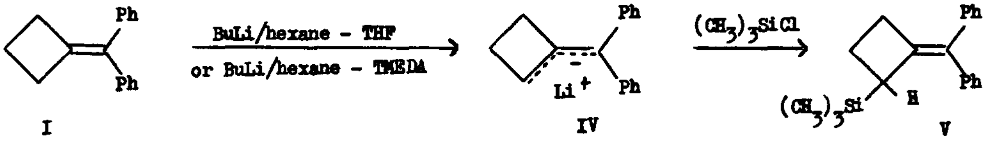
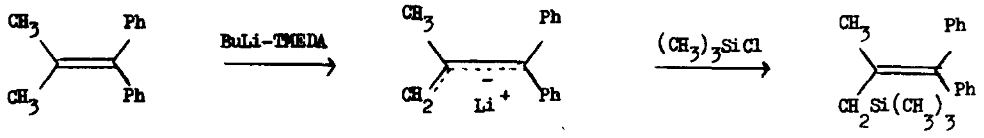
The reaction of BuLi and other metalation agents with arylmethanes and phenylallyl systems has been studied extensively during the last years. The generated anions have been trapped and analyzed by NMR[1].

We investigated the reaction of BuLi with diphenylmethylenecyclobutane (I)[2], diphenylmethylenecyclopropane (II)[3] and α-cyclopropylstyrene (III)[4], in order to evaluate the influence of the small rings on possible anion formations in these systems.

Excess of BuLi-TMEDA (tetramethylethylenediamine) complex[5] was added under nitrogen to I cooled to -100°. The reaction mixture was left to warm up to room temperature and after 2 hours at 25° the crystalline salt IV precipitated. The liquid phase was removed with a syringe and the solid was washed with hexane, dissolved in THF and its NMR spectrum recorded. The aromatic portion of the spectrum consists of three multiplets with integrated intensities of 2:2:1. First order analysis gives chemical shifts of 7.18/d, 6.81/d x d and 6.20/t for the ortho, meta and para protons respectively with j_{o-m} = 8 cps and j_{m-p} = 6.5 cps. This pattern is very similar to that reported for triphenylmethyllithium[1]. The upfield shift of the aromatic protons reflects the delocalization of the negative charge into the phenyl rings[1,6]. The same reaction was also accomplished with BuLi in hexane/THF mixture. The anion IV was reacted with trimethylsilylchloride in hexane to produce V, b.p. 170-175°/0.3 (ball oven) in 75% yield; NMR (CCl_4): 7.27/m, 10H (phenyl); 3.35-1.65, 5H (ring protons); 0.05/s, 9H (trimethylsilyl) and MS: M^+ 292 m/e.



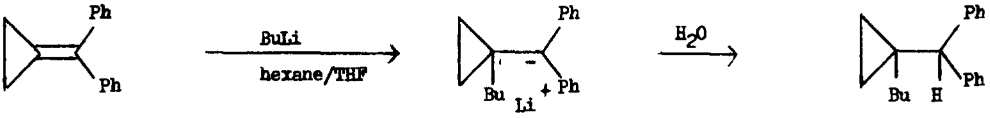
For comparison the metalation of the acyclic analog, 1,1-dimethyl-2,2-diphenylethylene (VI) was performed as described for I. Only with the BuLi-TMEDA complex were good yields of metalation product obtained; the reaction with BuLi in hexane/THF was much slower.



VI VII VIII

The aromatic part of the NMR spectrum of the anion VII in THF was very similar to that of IV and consisted of the following absorptions: 7.25/d (j = 8); 6.80/d x d (j_1 = 8, j_2 = 6.5) and 6.21/t (j = 6.5) for the ortho, meta and para protons respectively. Reaction of VII with trimethylsilylchloride gave VIII, b.p. 170-180°/0.2 (ball oven) in 90% yield; NMR (CCl_4): 7.3/bs, 10H (phenyl); 2.05/s, 5H (CH_3- + -CH_2-); 0.25/s, 9H (trimethylsilyl) and MS: M^+ 280 m/e. Attempts to prepare a dianion from VI by longer reaction times failed.

The metalation of I proceeds in the normal manner, as that of VI, to produce the anions IV and VII in high yield. There is no difficulty in introducing a second sp^2 carbon into I by proton abstraction. However, this cannot be achieved with the lower homolog-diphenylmethylenecyclopropane (II). Reaction of II with BuLi in hexane/THF proceeded with addition of BuLi to the double bond accompanied by extensive polymerization (use of BuLi-TMEDA complex caused even more polymerization). Quenching of the reaction mixture with water gave X, b.p. 180-190°/0.2 (ball oven) in 30% yield.

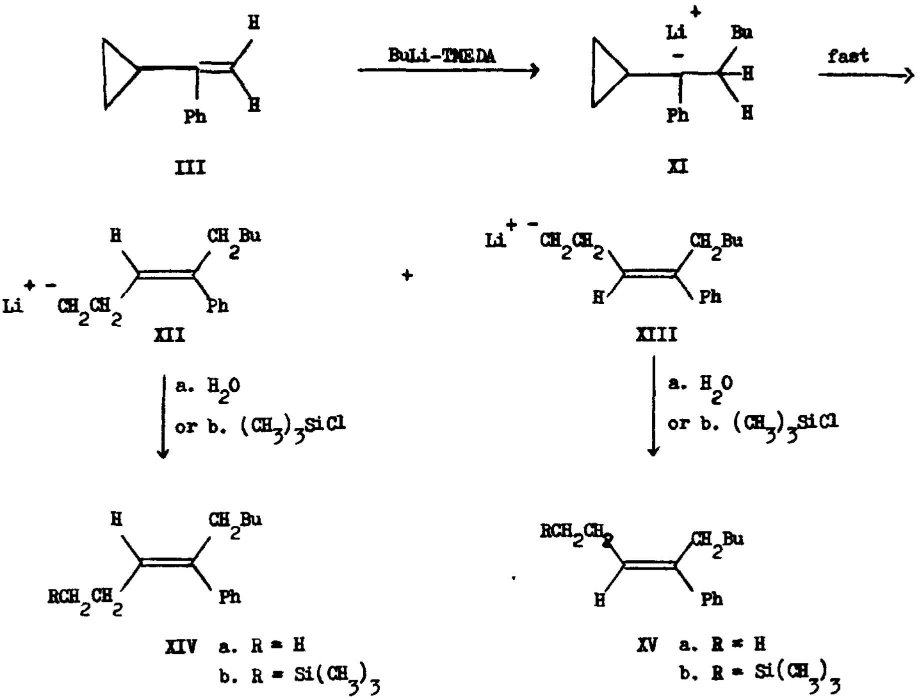


II IX X

The product was purified by GLC (SE 30, 15%, 2 m at 210°) and its structure was proven by spectrographic means. NMR (CCl_4): 7.03/m, 10H (phenyl); 4.16/s, 1H (benzhydryl); 1.30/m, 6H (-$CH_2CH_2CH_2$-); 0.80/t (j = 6), 3H (CH_3-); 0.29/s, 4H (cyclopropyl) and MS: m/e 264 (M^+, 7%) and 167 (Ph_2CH^+, 100%).

The absence of metalation in the case of II may be rationalized by the difficulty of introducing a second sp^2 carbon into the methylenecyclopropane skeleton, thus addition to the double bond is the preferred reaction. The negative charge in the carbanion IX is delocalized into the phenyl rings and this probably prevents IX from rearranging with ring-opening as might be expected$^{7)}$.

We were also interested in the influence of a cyclopropyl ring α to the double bond of a styrenic system on the reaction with BuLi. For this purpose we reacted the BuLi-TMEDA complex with α-cyclopropylstyrene (III).



The reaction was performed as described for I but the reaction mixture was left for only 30 min. at room temperature. The NMR spectrum of the clear red solution revealed a narrow band for the aromatic protons and a multiplet in the vinylic region (6.0-5.0). This pattern is in accord with the presence of anions XII and XIII. Addition of water to the reaction mixture gave mainly a mixture of XIVa and XVa, b.p. 80-85°/0.5 in 85% yield. The two isomers in a ratio 1.0:1.1 were separated by GLC (SE 30, 15%, 2 m at 170°)8). The structure of both 1-pentyl-cis-1-phenylbutene (XIVa) and 1-pentyl-trans-1-phenylbutene (XVa) was established from their NMR, UV and mass spectra.

XIVa: NMR (CCl_4): 7.0/m, 5H (phenyl); 5.30/t (j = 7), 1H (vinyl); 2.20/t (j = 6), 2H ($Ph-\overset{\shortparallel}{C}-CH_2-$); 1.87/quint. (j = 7), 2H ($Ph-\underset{|}{C}=\underset{|}{C}-CH_2-$); 1.5-0.6, 12H $[-(CH_2)_3CH_3 + CH_3-]$; UV: λ_{max}^{EtOH} (nm) 235 (ε 7,000) and MS: M^+ 202 m/e.

XVa: NMR (CCl_4): 7.0/bs, 5H (phenyl); 5.40/t (j = 7), 1H (vinyl); 2.35/m, 2H ($Ph-\overset{\shortparallel}{C}-CH_2-$); 2.10/quint. (j = 7), 2H ($Ph-\underset{|}{C}=\underset{|}{C}-CH_2-$); 1.4-0.6, 12H $[-(CH_2)_3CH_3 + CH_3-]$; UV: λ_{max}^{EtOH} (nm) 245 (ε 10,000) and MS: M^+ 202 m/e.

The distinction between the cis and trans geometry of XIVa and XVa was based on the difference of the chemical shift of the vinylic proton. The proton cis to the phenyl ring absorbs at a lower field (5.40 δ) than the proton located trans to the ring (5.30 δ)9). This assignment was confirmed by the difference of their UV spectra. The cis and trans isomers absorb at a different wavelength and have different extinctions as was shown for similar systems10).

Reaction of XII and XIII with trimethylsilylchloride gave XIVb and XVb. The silyl derivatives were separated by GLC (SE 30, 15%, 2 m at 190°) and their structure established by NMR in comparison with XIVa and XVa respectively.

<u>XIVb</u>: NMR (CCl_4): 7.20/m, 5H (phenyl); 5.50/t (j = 7), 1H (vinyl); 2.45/m, 2H ($\text{Ph-}\underset{\|}{C}\text{-CH}_2\text{-}$); 2.08/q (j = 7) 2H ($\text{Ph-}\underset{|}{C}\text{=}\underset{|}{C}\text{-CH}_2\text{-}$); 1.6-0.5, 11H [$-(CH_2)_3CH_3$ + $SiCH_2-$]; 0.15/s, 9H (trimethylsilyl).

<u>XVb</u>: NMR (CCl_4): 7.25/m, 5H (phenyl); 5.62/t (j = 7), 1H (vinyl); 2.60/m, 2H ($\text{Ph-}\underset{\|}{C}\text{-CH}_2\text{-}$); 2.42/q (j = 7), 2H ($\text{Ph-}\overset{|}{C}\text{=}\underset{|}{C}\text{-CH}_2\text{-}$); 1.6-0.8, 11H [$-(CH_2)_3CH_3$ + $SiCH_2-$]; 0.25/s, 9H (trimethylsilyl).

The formation of XII and XIII is rationalized by a stepwise mechanism. Addition of BuLi to the double bond of III generates XI which ring-opens[6,7] rapidly to yield XII and XIII. The formation of XI via addition of BuLi to an activated vinylcyclopropane system could be a general method to produce lithium salts of this type. Direct metalation of cyclopropylarylmethanes can be achieved only under drastic conditions with potassium and sodium reagents[6].

The scope and synthetic applications of this reaction are under current investigation.

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