

The Influence of Solvation of the Reactions of an Allylic Carbanion

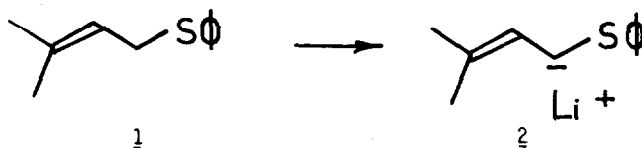
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The reaction of allylmagnesium and allyllithium derivatives with carbonyl compounds occurs with inversion of the allyl unit (1,2,3). Two explanations, a reaction involving a cyclic transition state or an S_{E2} reaction (2) have been presented for this behavior.

Suspecting that such regioselective reactions of allylic anions may depend on the nature of the ion pairs present (4), we undertook a study of the reactions of the stabilized allyllithium 2 in presence of different solvating species. This particular allyllithium 2 was chosen because of its stability in strongly solvating media. Furthermore it has the advantage of being stereochemically fixed in the E-geometry at the α,β -bond; the Z geometry being destabilized by steric interaction of the methyl group.

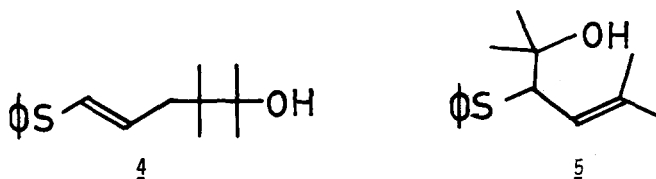


In addition to the reaction with a ketone acetone, alkylations with methyl iodide, allylbromide and dimethylallyl bromide were examined. The carbanion 2 was prepared by addition of one equivalent of n-butyllithium to a solution of 1 in tetrahydrofuran (THF) (5). The complexing agents: diazabicyclooctane (DABCO), N,N,N',N'-tetramethylethylene diamine (TMEDA), hexamethylphosphotriamide (HMPT) and the macrobicyclic diamino polyether [2,2,2] (6) were then added. After 30 min, these solutions were treated with an excess of reagent. The results are presented in Table 1.

To prove that the alcohols 4 and 5 obtained are the kinetic products*, alcohol 4 in THF was treated at -78°C with butyllithium in the presence

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* Equilibration of related alcoholates have been detected at higher temperatures (3).







of [2,2,2] and after 3 h water was added : alcohol 5 was not detected. Similarly the alcohol 5 in THF was treated at -78°C with butyllithium in the presence of DABCO and after 3 h water was added, no alcohol 4 was detected.

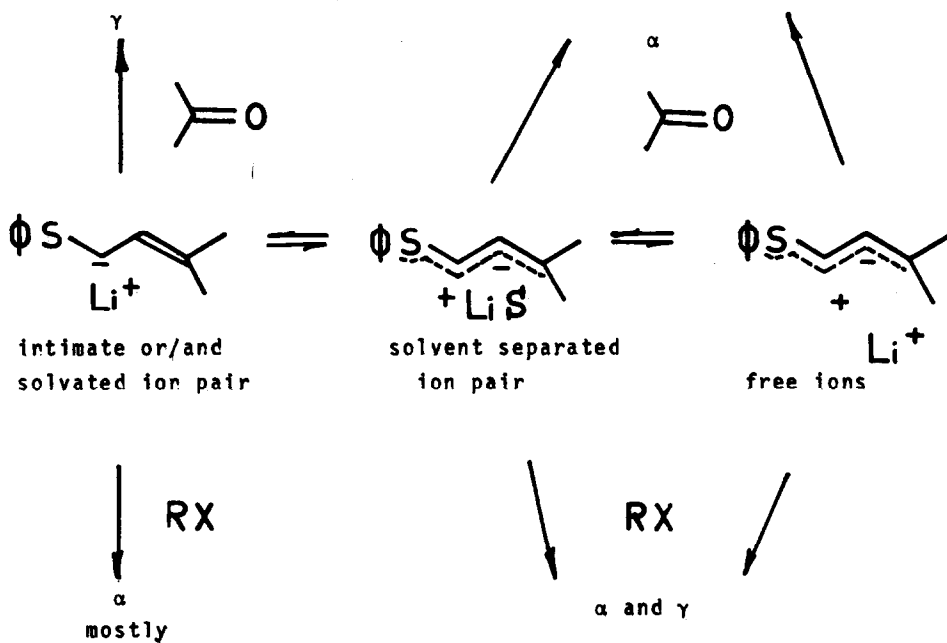
The results in Table 1 show clearly that the regioselectivity of alkylations and of reaction with acetone depends on the presence of solvating species. The results are best explained by assuming that in THF solution without a complexing agent or DABCO or TMEDA, the carbanion exists as an ion pair, the lithium ion closely associated with the α -carbon, like other allyllithium (8). This type of structure explains the fact that no isomerisation of the β,γ double bond is observed in very similar systems (9). The absence of isomerisation at β,γ double bond is a unique feature. The other allyllithium gives an equilibrium mixture : this explained by the reversible isomerisation of allyllithium with the lithium at the α -carbon to the allyllithium with the lithium at the γ -carbon, usually not detected. The reactivity with methyl iodide, allyl- and dimethylallylbromides is highest at the α -carbon ; with acetone the reaction occurs at the γ -carbon. The difference of regioselectivity of the reaction with acetone in THF or in THF-TMEDA is not reflected in the alkylation (not reported here) : the species present in these two media could be different. In the presence of HMPT, a good solvating agent, the carbanion is less associated with the cation, and the reactivity of the α -carbon towards acetone is enhanced. The cryptate [2,2,2] accomodates the lithium in its cavity so that solvent separated ion pairs or free anions are present (6). The reaction now occurs at both α and γ carbons with methyl iodide and at the α -carbon with acetone. The regioselectivity depends on the nature of the electrophile, due to steric or/and electronic factors. In presence of [2,2,2], beside the reaction products, we isolate starting material. This could be due to the enhancement of the reactivity of the carbanion which reacts then with solvent (10).

In conclusion, the classical allylic inversion mechanism probably involves only certain types of ion pairs : intimate ion pair or/and solvated ion pair. The control of the regioselectivity of the reactions of carbanion 2 by the solvation of its conterion may have applications in synthesis.

Table 1

Temperature	Complexing agent	Reagent	Yield	Proportion of reaction at the		References
				α carbon	γ carbon	
-20°	DABCO	MeI	100%	99	1	(5)
	"	Br- 	100%	87	12	(5)
	"	"	100%	94	6	(5)
	"		100%	-	100	(7)
-78°	none	MeI	100%	95		
	HMPT	"	100%	98	Traces	
	[2,2,2]	"	80%	60	40	
	[2,2,2]	Br- 	60%	50	50	
	none		100%	25	75	
	TMEDA	"	100%	Traces	90	
	HMPT	"	100%	40	60	
	[2,2,2]	"	60%*	100	0	(7)

* remaining starting material.



S: solvent or complexing agent.

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- (7) RMN Spectrum for 4 (CDCl_3) δ = 1,10 ppm (6H), 1,19 ppm (6H), 6,18 ppm (2H), 7,30 ppm (5H) ; with $\text{Eu}(\text{FOD})_3$ J vinylic = 15 Hz (trans) ; for 5 (CDCl_3) δ = 1,31 ppm (9H), 1,70 ppm (3H), 3,90 ppm (1H), d, J = 11 Hz, 5,27 ppm, d of m, 7,30 ppm (5H). Analytical data and mass spectrum in agreement with the proposed structures.
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