

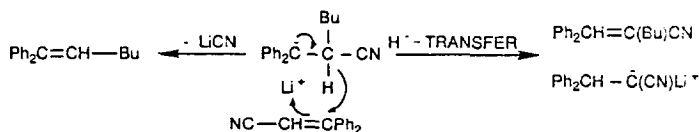
A Hydride Transfer Reaction from Salts of Carbanions to Activated Olefins

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Abstract. A novel reaction - a β -elimination of a hydride ion from carbanion salts RM (R = Li, MgBr) and $R_2N^-Li^+$, and its transfer to tetra-substituted activated olefins of the type $Ar_2C=C(CN)CO_2R$ (R= Me,Et), was studied. Yields of the reduced H^- -acceptor were used to follow the extent of the H^- -transfer reaction. A competing Michael addition reaction of RM to the activated olefin also took place. The effects of the solvation properties of the solvent, the reaction temperature, the positive counter-ion, and of various structural features of the H^- -donor and the H^- -acceptor, were studied. Structural factors associated with both reactants, played a critically significant role due to the bimolecularity of the reaction. A benzyl substituent at C_β of RM, a methine-type β -carbon, or a small size of R of RM, resulted in a relatively high extent of the H^- -transfer reaction. It is suggested that the presently studied β -elimination of a hydride ion takes place by a bimolecular E_{2cB} -type mechanism.

A recent report on the $Ph_2C=CH-CN - n-BuLi$ reaction system¹ carried out in THF (Scheme 1) suggests that a hydride-transfer reaction from the carbanionic intermediate to the activated olefin, might be a side reaction (which has not yet been accounted for) in Michael addition reaction systems:



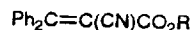
Scheme 1

β -Eliminations of hydride ions² from salts of alkoxides³, amide anions^{4,5}, and carbanions^{6,7}, affected by their transfer to non-enolizable ketones and aldehydes to yield the corresponding carbonyl compounds, ketimines and alkenes, respectively, have been reported. Reetz⁷ studied in detail transfer reactions of hydride ions from carbanion salts to boranes and carbonium salts. Hydride-transfer reactions from alkoxides^{3d} and amide⁸ salts to olefins, have been reported in very few cases. A hydride-transfer from lithium amides having $C_\alpha-H$ bonds to tetra-substituted activated olefins, has been applied as a method of reduction of such olefins⁹.

The results of a preliminary-type study of a novel hydride-transfer reaction from RM salts (M = Li, MgBr) to activated olefins, are reported. The effects of the solvating properties of the reaction medium, and - of structural features of the H^- -donors and the H^- -acceptors involved, on such reactions, were studied.

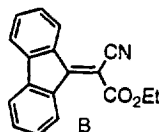
RESULTS AND DISCUSSION

Two β,β -diaryl derivatives of methylene alkyl cyanoacetate, **A** and **B**, were used as H^- -acceptors:

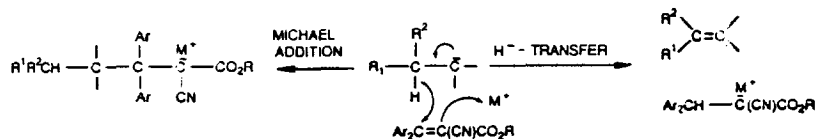


A: R=Me

A': R=Et



Tetra-substituted activated olefins were used in order to avoid vinyl carbanion formation¹⁰, and to suppress the nucleophilic addition of RM to the activated olefins. However, products of both the H^- -transfer reaction and the Michael addition reaction were formed in the reaction systems studied (scheme 2):



Scheme 2

The extent of the presently studied H^- -transfer reactions was followed by determining the yields of the reduced derivatives of the olefinic H^- -acceptors.

The feasibility of hydride-transfer reactions of this type was tested by using as an H^- -donor, an organolithium compound which was incapable (due to steric hindrance) of adding to the olefinic H^- -acceptors used. The addition product of $n\text{-BuLi}$ to 1,1-diphenyl ethylene (DPE)¹¹, $CH_3(CH_2)_3C(Ph)_2Li^+$ prepared in situ, was used. This addition could be carried out to completion in either diethyl ether (DEE) or in THF, on using the appropriate reaction conditions (Table 1). Olefin **A'** was added to the deep-red solution of the $n\text{-BuLi}$ - DPE reaction mixture. The major products were those of the H^- -transfer reaction from $n\text{-Bu-CH}_2\text{-C(Ph)}_2Li^+$ to **A'**, namely - 1,1-diphenyl-hex-1-ene, and **A'H**₂, the saturated derivative of the olefin **A'** (Table 1). The fact that the yields of these two products were about the same, suggests that the hydride transfer reaction from the Michael addition intermediate $n\text{-Bu-CH}_2\text{-C(Ph)}_2Li^+$ to the activated olefin **A'** (and not to DPE), is by far the dominant one.

The effect of solvent on the extent of the H^- -transfer reaction from RM (R = $n\text{-Bu}$; M = Li, MgBr) to olefins **A** and **B** was studied in a poorly solvating medium - DEE, and in a relatively good one - THF. The products isolated were the corresponding reduced olefins - **AH**₂ and **BH**₂, and the Michael addition products, $n\text{-Bu-AH}$ and $n\text{-Bu-BH}$. The results (Table 2) clearly indicate that the effect of solvent depends on the type of the positive counter-ion M of RM. The yields of **AH**₂ and **BH**₂ in the $n\text{-BuLi}$ - **A** and in the $n\text{-BuLi}$ - **B** reaction systems, respectively, were higher in THF as compared to DEE, whereas DEE was more effective than THF when using $n\text{-BuMgBr}$ as the H^- -donor. The results obtained on using $n\text{-BuLi}$ as the H^- -donor are obviously due to the fact that the $R^-, Li^+ \rightleftharpoons R \parallel Li^+$ equilibrium in DEE

Table 1. The n-BuLi - CH₂=CPh₂ - Ph₂C=C(CN)CO₂Et Reaction System

[n-BuLi] (mmol)	[DPE] (mmol)	[A'] ^a (mmol)	Solvent	temp. (C°)	Reaction time (h)	Yields of Products (%)				
						DPE	BuCH ₂ CHPh ₂	BuCH=CPh ₂	Δ'H ₂ ^a	BuΔ'H ^d
10	10	-	DEE	-78	0.25		0			
10	10	-	DEE	-78	4.5		0			
10	10	-	DEE	0	0.25		45			
10	10	-	DEE	0	1		78			
10	10	-	DEE	23	0.25		94			
10	10	-	THF	-78	0.25		93			
10	10	-	THF	0	0.25		84			
10	10	-	THF	0	1		85			
3.2	3	4	DEE	23	2.5	3.2	16	32	43	4
3.2	3	4	THF	-78	7.5	2.2	<i>b</i>	48	45	<i>b</i>
3.2	3	4	THF	0	7.5	1.6		47	43	<i>b</i>
3.2	3	4	THF	23	2	4.1	15	36	35	<i>b</i>
3.2	3	4	THF-DME ^c	-78	1	12	8	38	41	<i>b</i>
3.2	3	4	THF-DME ^c	0	4	18	6.5	37	33	<i>b</i>
3.2	3	4	THF-DME ^c	23	2	27.4	9.2	22	27	<i>b</i>

a Δ': Ph₂C=C(CN)CO₂Et ; Δ'H₂: Ph₂CH-CH(CN)CO₂Et ; BuΔ'H: Ph₂C(n-Bu)-CH(CN)CO₂Et.

Δ, ΔH₂, and BuΔH in the following tables are the corresponding methyl esters.

b traces only were detected

c The solvent mixture contained 10% by volume of DME (1,2-dimethoxyethane).

is practically all to the side of the chemically much less reactive contact ion-pairs, while the equilibrium concentration of the more reactive solvent-separated ion-pairs is relatively high in better solvating solvents such as THF, dimethoxy ethane, etc.¹². The ratio of the Schlenk equilibrium^{13a,14} (eq.1) constants measured for several "RMgX" compounds (R=Me, Et, Ph; X=Cl, Br, I), in DEE and in THF, is $K_{DEE}/K_{THF} \approx 10^2$ ^{13b,15}, indicating that RMgX is by far the major component of the equilibrium mixture in DEE. This fact, combined with the observed opposite trend of the solvent effect on the n-BuMgBr - A reaction system as compared to the n-BuLi - A and B reaction systems (Table 2), suggest that RMgX is a much more effective H⁻-donor as compared to R₂Mg.

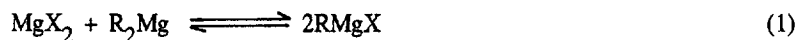


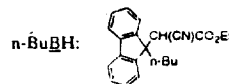
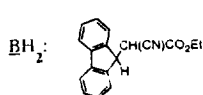
Table 2. Effect of Solvent on the H⁻-Transfer Reaction^a

M of n-BuM	mmol	H ⁻ -Acceptor	mmol	Solvent	Reaction temp. (C°)	Reduction product	Yield (%)	Addition product	Yield (%)
Li	3.20	<u>A</u>	3.50	DEE	-78	ΔH_2^b	0	Bu ΔH^b	0
Li	3.20	<u>A</u>	3.50	THF	-78	ΔH_2	19	Bu ΔH	19.5
Li	3.20	<u>A</u>	3.50	DEE	0	ΔH_2	1.3	Bu ΔH	53
Li	3.20	<u>A</u>	3.50	THF	0	ΔH_2	7	Bu ΔH	29.4
Li	3.52	<u>B</u>	3.50	DEE	0	$\underline{B}H_2^b$	15	Bu $\underline{B}H^b$	51
Li	15.04	<u>B</u>	4.98	DEE	0	$\underline{B}H_2$	28.3	Bu $\underline{B}H$	71.7
Li	15.04	<u>B</u>	4.98	THF	0	$\underline{B}H_2$	39.4	Bu $\underline{B}H$	60.6
MgBr	1.98	<u>A</u>	2.02	DEE	0	ΔH_2	10	Bu ΔH	18
MgBr	2.10	<u>A</u>	2.05	THF	0	ΔH_2	0	Bu ΔH	10
MgBr	1.98	<u>A</u>	2.02	DEE	23	ΔH_2	15.5	Bu ΔH	18
MgBr	2.10	<u>A</u>	2.05	THF	23	ΔH_2	0	Bu ΔH	16
MgBr	14.85	<u>A</u>	4.98	DEE	23	ΔH_2	41	Bu ΔH	46.7
MgBr	14.85	<u>A</u>	4.98	THF	23	ΔH_2	15.8	Bu ΔH	47.6

^a Experimental conditions for the experiments listed in this and the following tables, are described in the Experimental Section.

^b ΔH_2 : $\text{Ph}_2\text{CH}-\text{CH}(\text{CN})\text{CO}_2\text{Me}$;

Bu ΔH : $\text{Ph}_2\text{C}(\text{n-Bu})-\text{CH}(\text{CN})\text{CO}_2\text{Me}$;



Intermolecular hydride-transfer reactions should obviously require an optimal mutual arrangement of the H-donor and the H-acceptor, in order to make the act of this transfer possible. It is therefore expected that structural features associated with each of the two participants will affect the extent of H-transfer reactions. The effect of the structure of R of the RM and - of the olefinic H-acceptor, were studied. The fluorene derivative B, because of its planarity, was expected to be a more efficient H-acceptor, as compared to the analogous non-planar and bulkier olefin A. The results of the experiments carried out in THF and in DEE at different temperatures indicate that the relative efficiencies of A and B as H-acceptors are influenced not only by their structural features, but are dependent on whether n-BuLi or n-BuMgBr is used as the H-donor (Table 3). Olefin B was a much more efficient H-acceptor (both in DEE and THF) as compared to A, when using n-BuLi as the H-donor. However, on using n-BuMgBr as the H-donor, and carrying out the reactions in DEE, it was found that olefin A was a much more effective H-acceptor as compared to B. This might be due to the fact that,

in general, reactions of RMgX are more sterically demanding as compared to RLi compounds¹⁶. The planarity of B, which presumably facilitates the formation of its properly-structured bimolecular transition state with $n\text{-BuLi}$, might not necessarily be an advantage in its reaction with $n\text{-BuMgBr}$. Olefin A, having a relatively much higher degree of flexibility (because of its $\text{C}_\beta\text{-Ph}$ free rotations), might be more efficient than olefin B in fitting itself into a bimolecular transition state with the more sterically-demanding $n\text{-BuMgBr}$.

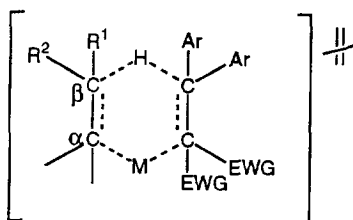
Table 3. Effect of Structure of the H^- -Acceptor on the H^- -Transfer Reaction

M of n-BuM	mmol	H^- -Acceptor	mmol	Solvent	Reaction temp. (C°)	Reduction product	Yield (%)	Addition product	Yield (%)
Li	3.20	<u>A</u>	3.5	DEE	0	AH_2	1.3	BuAH	53
Li	3.52	<u>B</u>	3.5	DEE	0	BH_2	15	BuBH	51
Li	3.20	<u>A</u>	3.5	DEE	23	AH_2	5.4	BuAH	53
Li	3.52	<u>B</u>	3.5	DEE	23	BH_2	19	BuBH	49
Li	15.04	<u>A</u>	4.98	DEE	23	AH_2	13.4	BuAH	86.6
Li	15.04	<u>B</u>	4.98	DEE	23	BH_2	23	BuBH	77
Li	3.20	<u>A</u>	3.5	THF	0	AH_2	7	BuAH	29.4
Li	3.52	<u>B</u>	3.58	THF	0	BH_2	20.6	BuAH	35.5
MgBr	1.98	<u>A</u>	2.02	DEE	0	AH_2	10	BuAH	18
MgBr	2.10	<u>B</u>	2.04	DEE	0	BH_2	0	BuBH	30
MgBr	1.98	<u>A</u>	2.02	DEE	23	AH_2	15.5	BuAH	18
MgBr	2.10	<u>B</u>	2.04	DEE	23	BH_2	0	BuBH	30
MgBr	14.85	<u>A</u>	4.98	DEE	23	AH_2	41	BuAH	46.7
MgBr	14.85	<u>B</u>	4.98	DEE	23	BH_2	15.1	BuBH	84.2

The effect of the structure of R of RM was studied by using the following alkyl magnesium bromides, RMgBr , as H^- -donors: R = Et, i-Pr, n-Bu, cyclohexyl, i-Bu, 3-phenylpropyl. The results obtained (Table 4) show that the effect that the R group of RMgBr has on the extent of the H^- -transfer reaction, is due to two different structural features of R - the type of the β -substituents R^1 and R^2 of the $\text{R}^1\text{R}^2\text{CH-CH}_2\text{MgBr}$ used, and the size (or shape) of the R group.

The highest extent of the H^- -transfer reaction was observed for i-BuMgBr and for $\text{Ph}((\text{CH}_2)_3\text{MgBr}$, in which two alkyl groups and a benzyl group, respectively, are attached to C_β . Development of a positive charge on C_β of the H^- -donor in the bimolecular transition state (Fig. 1), must have taken place during the cleavage of the $\text{C}_\beta\text{-H}$ bond. It might therefore be suggested that the

relatively high extent of the H-transfer reaction observed for these two H-donors, is due to stabilization of the transition state affected by the combined inductive effects of the two methyl groups at C $_{\beta}$ of the *i*-BuMgBr, and - to the hyperconjugative effect of the β -benzyl group in Ph(CH $_2$) $_3$ MgBr (resonance structures of the type PhCH $_2$ CH $_2$ CH $_2$ MgBr). This implies, that in such hydride-transfer reactions, the C $_{\beta}$ -H bond-cleavage takes place in the rate-determining step.



(Fig. 1)

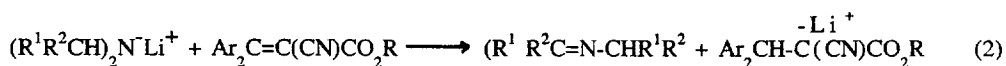
The extent of the H-transfer reaction decreased with increasing the size of the R of RMgBr as follows: *n*-R, % $\underline{\text{AH}}_2$: Et, 24; *n*-Bu, 13; *n*-dodecyl, 1-2 (Table 4). This observation is also in accord with the assumed bimolecularity of the presently studied reaction. The relatively high yield of $\underline{\text{AH}}_2$ (24%) obtained in the EtMgBr - $\underline{\text{A}}$ - DEE reaction system, seems at first sight to be a contradictory result with regard to the above-mentioned effect of alkyl substitution at C $_{\beta}$. It turns out that in this case, due to the bimolecularity of the reaction, the compactness of the ethyl group compensates for the relatively low stabilization of the transition state.

Table 4. Effect of Structure of R of RM on the H $^-$ - Transfer Reaction

R of RMgBr	mmol	H-Acceptor	mmol	Reaction time(h)	Solvent	Reduction Product	Yield (%)	Addition product	Yield (%)
CH $_3$ CH $_2$	2.68	$\underline{\text{A}}$	2.7	2	DEE	$\underline{\text{AH}}_2$	24	Et $\underline{\text{A}}\text{H}$	30.4
<i>n</i> -C $_4$ H $_9$	4.50	$\underline{\text{A}}$	5	2	DEE	$\underline{\text{AH}}_2$	13	<i>n</i> -Bu $\underline{\text{A}}\text{H}$	13.2
(CH $_3$) $_2$ CH	6	$\underline{\text{A}}$	2	14	DEE	$\underline{\text{AH}}_2$	2.5	-	-
C $_6$ H $_{11}$	4.23	$\underline{\text{A}}$	5	4	DEE	$\underline{\text{AH}}_2$	1-2	C $_6$ H $_{11}\underline{\text{A}}\text{H}$	-
<i>n</i> -C $_{12}$ H $_{25}$	2.50	$\underline{\text{A}}$	2.4	2	DEE	$\underline{\text{AH}}_2$	1-2	<i>n</i> -C $_{12}$ H $_{25}\underline{\text{A}}\text{H}$	1-2
(CH $_3$) $_2$ CHCH $_2$	2.30	$\underline{\text{A}}$	2.02	2	DEE	$\underline{\text{AH}}_2$	22.2	<i>i</i> -Bu $\underline{\text{A}}\text{H}$	11
(CH $_3$) $_2$ CHCH $_2$	4.6	$\underline{\text{A}}$	4.3	2.5	DEE	$\underline{\text{AH}}_2$	25.3	<i>i</i> -Bu $\underline{\text{A}}\text{H}$	3.9
(CH $_3$) $_2$ CHCH $_2$	14.7	$\underline{\text{A}}$	4.98	2	DEE	$\underline{\text{AH}}_2$	58.1	<i>i</i> -Bu $\underline{\text{A}}\text{H}$	18.3
<i>n</i> -C $_4$ H $_9$	14.85	$\underline{\text{A}}$	4.98	2	DEE	$\underline{\text{AH}}_2$	41	<i>n</i> -Bu $\underline{\text{A}}\text{H}$	46.7
Ph(CH $_2$) $_3$	3.25	$\underline{\text{A}}$	3.80	3.75	DEE	$\underline{\text{AH}}_2$	24	Ph(CH $_2$) $_3\underline{\text{A}}\text{H}$	22
Ph(CH $_2$) $_3$	10	$\underline{\text{A}}$	4.56	2	DEE	$\underline{\text{AH}}_2$	59	Ph(CH $_2$) $_3\underline{\text{A}}\text{H}$	41

A parallel study was carried out using lithium salts of secondary amides ($(R^1R^2CH)_2N^+Li^-$) as H^- -donors, in order to provide additional experimental data in support of the above presented explanations regarding the effects of structural factors associated with the H^- -donor and the H^- -acceptor, on the extent of the H^- -transfer reaction studied.

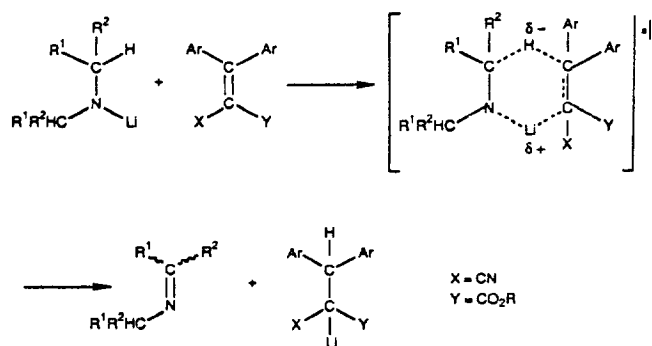
The hydride-transfer reaction which took place in the $(R^1R^2CH)_2N^+Li^-$ - activated olefin reaction system, in THF at $-78^\circ C$, resulted in two products - the reduced olefin and the corresponding ketimine (eq. 2):



The extent of the H^- -transfer reaction was determined by quantitatively isolating the reduced activated olefin. Isolation of the other reaction product, the ketimine derivatives, was difficult in most cases, due to its facile hydrolytic decomposition to the corresponding amine and ketone. The planar fluorene derivatives **B** was a much more effective H^- -acceptor as compared to the diphenyl derivative **A** (Table 5). This result was in line with that observed for $n-BuLi$ as an H^- -donor (Table 3).





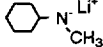
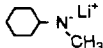


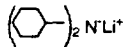
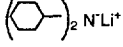
As to the effect of R of RM, the extent of this hydride-transfer reaction was very much affected by type of the substituents R^1 and R^2 attached to the β -atom of the amide salt. Relatively high yields of \underline{AH}_2 were obtained only when both R^1 and R^2 were alkyl groups as in $(i-Pr)_2N^+Li^-$ and in $(\text{Cyclohexyl})_2N^+Li^-$. Combinations of $R^1 = Ph$ and $R^2 = H$, or - $R^1 = \text{alkyl}$, $R^2 = H$, were much less effective. In support of, and in line with the above presented conclusion, it might be assumed that a bimolecular transition state, in which a positive charge is being developed at the C_α of the lithium amide, is also involved in the rate-determining step of this H^- -transfer reaction, which may be schematically described as follows (Scheme 3):


The bimolecular nature of the presently studied H^- -transfer reactions, has been clearly demonstrated through the effects which the various structural factors (associated with the two reactants involved) have on the extent of the H^- -transfer reactions studied. Substituent effects suggest that the $C_\beta-H$ bond-cleavage is the rate-determining step of the reaction. The mechanism of



Scheme 3

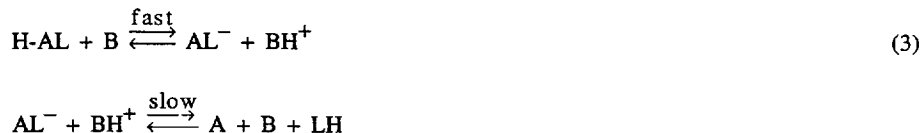
**Table 5. The $(R^1R^2CH)_2N^-Li^+$ - Activated Olefin Reaction System.
Effect of Structural Factors^a**

$(R^1R^2CH)_2N^-Li^+$	Activated Olefin	Reduction Product	Yield (%)
$(PhCH_2)_2N^-Li^+$	A'	A' H ₂	0
$(PhCH_2)_2N^-Li^+$	B ^b	B H ₂	17
	A'	A' H ₂	0
	B	B H ₂	5.2
	A'	A' H ₂ ^c	0
	B	B H ₂	24
	A' ^d	A' H ₂	3.6
	B	B H ₂	17
	A'	A' H ₂	1-2
	B	B H ₂	19
$[(CH_3)_2CH]_2N^-Li^+$	A'	A' H ₂	79
$[(CH_3)_2CH]_2N^-Li^+$	A' ^e	A' H ₂	67
$[(CH_3)_2CH]_2N^-Li^+$	B	B H ₂	85
	A' ^f	A' H ₂	40
	B	B H ₂	44

- ^a The reactions were carried in THF at -78°C. 6 mmol of the lithium amide and 2 mmol of the activated olefin were used. Reaction time 30 min. Total volume of reaction mixture was 150 ml.
- ^b 6.24 mmol of $(PhCH_2)_2N^-Li^+$ and 1.7 mmol of B, were used.
- ^c Most of the product¹ isolated was the amide derived from A, $Ph_2C=C(CN)-C(=O)-N$ 
- ^d ^e ^f ^g ^h ⁱ ^j ^k ^l ^m ⁿ ^o ^p ^q ^r ^s ^t ^u ^v ^w ^x ^y ^z ^{aa} ^{ab} ^{ac} ^{ad} ^{ae} ^{af} ^{ag} ^{ah} ^{ai} ^{aj} ^{ak} ^{al} ^{am} ^{an} ^{ao} ^{ap} ^{aq} ^{ar} ^{as} ^{at} ^{au} ^{av} ^{aw} ^{ax} ^{ay} ^{az} ^{ba} ^{bb} ^{bc} ^{bd} ^{be} ^{bf} ^{bg} ^{bh} ^{bi} ^{bj} ^{bk} ^{bl} ^{bm} ^{bn} ^{bo} ^{bp} ^{bq} ^{br} ^{bs} ^{bt} ^{bu} ^{bv} ^{bw} ^{bx} ^{by} ^{bz} ^{ca} ^{cb} ^{cc} ^{cd} ^{ce} ^{cf} ^{cg} ^{ch} ^{ci} ^{cj} ^{ck} ^{cl} ^{cm} ^{cn} ^{co} ^{cp} ^{cq} ^{cr} ^{cs} ^{ct} ^{cu} ^{cv} ^{cw} ^{cx} ^{cy} ^{cz} ^{da} ^{db} ^{dc} ^{dd} ^{de} ^{df} ^{dg} ^{dh} ^{di} ^{dj} ^{dk} ^{dl} ^{dm} ^{dn} ^{do} ^{dp} ^{dq} ^{dr} ^{ds} ^{dt} ^{du} ^{dv} ^{dw} ^{dx} ^{dy} ^{dz} ^{ea} ^{eb} ^{ec} ^{ed} ^{ee} ^{ef} ^{eg} ^{eh} ^{ei} ^{ej} ^{ek} ^{el} ^{em} ^{en} ^{eo} ^{ep} ^{eq} ^{er} ^{es} ^{et} ^{eu} ^{ev} ^{ew} ^{ex} ^{ey} ^{ez} ^{fa} ^{fb} ^{fc} ^{fd} ^{fe} ^{ff} ^{fg} ^{fh} ^{fi} ^{fj} ^{fk} ^{fl} ^{fm} ^{fn} ^{fo} ^{fp} ^{fq} ^{fr} ^{fs} ^{ft} ^{fu} ^{fv} ^{fw} ^{fx} ^{fy} ^{fz} ^{ga} ^{gb} ^{gc} ^{gd} ^{ge} ^{gf} ^{gg} ^{gh} ^{gi} ^{gj} ^{gk} ^{gl} ^{gm} ^{gn} ^{go} ^{gp} ^{gq} ^{gr} ^{gs} ^{gt} ^{gu} ^{gv} ^{gw} ^{gx} ^{gy} ^{gz} ^{ha} ^{hb} ^{hc} ^{hd} ^{he} ^{hf} ^{hg} ^{hh} ^{hi} ^{hj} ^{hk} ^{hl} ^{hm} ^{hn} ^{ho} ^{hp} ^{hq} ^{hr} ^{hs} ^{ht} ^{hu} ^{hv} ^{hw} ^{hx} ^{hy} ^{hz} ^{ia} ^{ib} ^{ic} ^{id} ^{ie} ^{if} ^{ig} ^{ih} ⁱⁱ ^{ij} ^{ik} ^{il} ^{im} ⁱⁿ ^{io} ^{ip} ^{iq} ^{ir} ^{is} ^{it} ^{iu} ^{iv} ^{iw} ^{ix} ^{iy} ^{iz} ^{ja} ^{jb} ^{jc} ^{jd} ^{je} ^{jf} ^{jj} ^{jk} ^{jl} ^{jm} ^{jn} ^{jo} ^{jp} ^{jq} ^{jr} ^{js} ^{jt} ^{ju} ^{kv} ^{kw} ^{kx} ^{ky} ^{kz} ^{la} ^{lb} ^{lc} ^{ld} ^{le} ^{lf} ^{lg} ^{lh} ^{li} ^{lj} ^{lk} ^{ll} ^{lm} ^{ln} ^{lo} ^{lp} ^{lq} ^{lr} ^{ls} ^{lt} ^{lu} ^{lv} ^{lw} ^{lx} ^{ly} ^{lz} ^{ma} ^{mb} ^{mc} ^{md} ^{me} ^{mf} ^{mg} ^{mh} ^{mi} ^{mj} ^{mk} ^{ml} ^{mm} ^{mn} ^{mo} ^{mp} ^{mq} ^{mr} ^{ms} ^{mt} ^{mu} ^{mv} ^{mw} ^{mx} ^{my} ^{mz} ^{na} ^{nb} ^{nc} nd ^{ne} ^{nf} ^{ng} ^{nh} ⁿⁱ ^{nj} ^{nk} ^{nl} ^{nm} ⁿⁿ ^{no} ^{np} ^{nq} ^{nr} ^{ns} ^{nt} ^{nu} ^{nv} ^{nw} ^{nx} ^{ny} ^{nz} ^{oa} ^{ob} ^{oc} ^{od} ^{oe} ^{of} ^{og} ^{oh} ^{oi} ^{oj} ^{ok} ^{ol} ^{om} ^{on} ^{oo} ^{op} ^{oq} ^{or} ^{os} ^{ot} ^{ou} ^{ov} ^{ow} ^{ox} ^{oy} ^{oz} ^{pa} ^{pb} ^{pc} ^{pd} ^{pe} ^{pf} ^{pg} ^{ph} ^{pi} ^{pj} ^{pk} ^{pl} ^{pm} ^{pn} ^{po} ^{pp} ^{pq} ^{pr} ^{ps} ^{pt} ^{pu} ^{pv} ^{pw} ^{px} ^{py} ^{pz} ^{qa} ^{qb} ^{qc} ^{qd} ^{qe} ^{qf} ^{qg} ^{qh} ^{qi} ^{qj} ^{qk} ^{ql} ^{qm} ^{qn} ^{qo} ^{qp} ^{qq} ^{qr} ^{qs} ^{qt} ^{qu} ^{qv} ^{qw} ^{qx} ^{qy} ^{qz} ^{ra} ^{rb} ^{rc} rd ^{re} ^{rf} ^{rg} ^{rh} ^{ri} ^{rj} ^{rk} ^{rl} ^{rm} ^{rn} ^{ro} ^{rp} ^{rq} ^{rr} ^{rs} ^{rt} ^{ru} ^{rv} ^{rw} ^{rx} ^{ry} ^{rz} ^{sa} ^{sb} ^{sc} ^{sd} ^{se} ^{sf} ^{sg} ^{sh} ^{si} ^{sj} ^{sk} ^{sl} sm ^{sn} ^{so} ^{sp} ^{sq} ^{sr} ^{ss} st ^{su} ^{sv} ^{sw} ^{sx} ^{sy} ^{sz} ^{ta} ^{tb} ^{tc} ^{td} ^{te} ^{tf} ^{tg} th ^{ti} ^{tj} ^{tk} ^{tl} tm ^{tn} ^{to} ^{tp} ^{tq} ^{tr} ^{ts} ^{tt} ^{tu} ^{tv} ^{tw} ^{tx} ^{ty} ^{tz} ^{ua} ^{ub} ^{uc} ^{ud} ^{ue} ^{uf} ^{ug} ^{uh} ^{ui} ^{uj} ^{uk} ^{ul} ^{um} ^{un} ^{uo} ^{up} ^{uq} ^{ur} ^{us} ^{ut} ^{uu} ^{uv} ^{uw} ^{ux} ^{uy} ^{uz} ^{va} ^{vb} ^{vc} ^{vd} ^{ve} ^{vf} ^{vg} ^{vh} ^{vi} ^{vj} ^{vk} ^{vl} ^{vm} ^{vn} ^{vo} ^{vp} ^{vq} ^{vr} ^{vs} ^{vt} ^{vu} ^{vv} ^{vw} ^{vx} ^{vy} ^{vz} ^{wa} ^{wb} ^{wc} ^{wd} ^{we} ^{wf} ^{wg} ^{wh} ^{wi} ^{wj} ^{wk} ^{wl} ^{wm} ^{wn} ^{wo} ^{wp} ^{wq} ^{wr} ^{ws} ^{wt} ^{wu} ^{wv} ^{ww} ^{wx} ^{wy} ^{wz} ^{xa} ^{xb} ^{xc} ^{xd} ^{xe} ^{xf} ^{yg} ^{yh} ^{yi} ^{yj} ^{yk} ^{yl} ^{ym} ^{yn} ^{yo} ^{yp} ^{yq} ^{yr} ^{ys} ^{yt} ^{yu} ^{yv} ^{yw} ^{yx} ^{yy} ^{yz} ^{za} ^{zb} ^{zc} ^{zd} ^{ze} ^{zf} ^{zg} ^{zh} ^{zi} ^{zj} ^{zk} ^{zl} ^{zm} ^{zn} ^{zo} ^{zp} ^{zq} ^{zr} ^{zs} ^{zt} ^{zu} ^{zv} ^{zw} ^{zx} ^{zy} ^{zz}

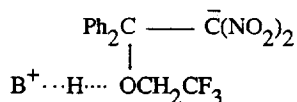
this β -elimination reaction of a hydride ion from salts of carbanions can therefore be neither of the E_1cB -type (for which a reversible or an irreversible formation of a stable carbanion is the rate-determining step)^{17,18}, nor even of the uncommon " E_1cB of the second type"¹⁹, for which the β -elimination of the anionic leaving group is the rate-determining step. The latter mechanism results from a combination of a stable carbanion and a poor leaving group at C_β .

A very uncommon electrophile-assisted elimination of an anion ($\text{CF}_3\text{CH}_2\text{O}^-$) from a relatively stable carbanion salt, may bear relevance to the presently studied hydride-transfer reactions (eq. 3):¹⁹



(A = $\text{Ph}_2\text{C}=\text{C}(\text{NO}_2)_2$; $\text{AL}^- = \text{Ph}_2\text{C}(\text{OCH}_2\text{CF}_3)\text{-}\bar{\text{C}}(\text{NO}_2)_2$; B = pyridine, collidine).

The reaction was first order in the carbanion AL^- and in the electrophile BH^+ , and was dependent on the type of B. It was suggested that it is an E_2cB -type elimination, having the following transition state for the assisted step:¹⁹



A close mechanistic analogy seems to exist between this reaction and the presently studied β -elimination of a hydride ion from carbanion salts. This analogy is based on: (a) the essential involvement of an electrophile (the olefinic H-acceptor) in the H-transfer reaction, (b) the observed dependence of the extent of the H-transfer reaction on the type of the electrophilic olefin, and (c) the observed effect of substituents on C_β of the carbanion salt. It might be therefore reasonably assumed that the presently studied β -elimination reactions of a hydride ion from carbanion salts assisted by an electrophilic olefin, might similarly have a bimolecular E_2cB -type mechanism, the transition state of which (Fig.1) bears analogy to that involved in the above mentioned reaction (eq.3).

EXPERIMENTAL

¹H-NMR spectra were measured with a Bruker 200 MHz spectrometer in CDCl_3 , using tetramethylsilane as an internal standard. All chemical shifts (δ) and coupling constants (J) values are in ppm and Hz units, respectively. Mass spectra were measured with a DuPont 21-491B spectrometer.

Materials. Diethylether (AR) and THF (AR) were refluxed over sodium wire and then distilled. A solution of sodium diphenyl ketyl in the distilled ether was prepared, and the required amount of the ether was distilled from this solution directly into the reaction flask. Ethyl bromide, n-butyl bromide, and iso-butyl bromide were dried over CaCl_2 and distilled before use. Fractions of these bromides having boiling points of 37-40°C/760 mmHg, 100-102°C/760 mmHg and 90-92°C/760 mmHg, respectively, were used. n-Dodecyl bromide (Aldrich, 98%) was used without any further purification. Alkyl bromides of the type $\text{PhCH}(\text{R})\text{Br}$ (R = Et, n-Pr, i-Pr) were prepared by bromination of the corresponding alkyl benzene with NBS²⁰. 3-Bromo-1-phenylpropane (Schuchardt, 99%) was used without any further purification. Secondary amines were dried over KOH and distilled before use. Fractions of

amines having the following boiling points were used: di-n-propyl amine (b.p. 83-84°C/760 mmHg), di-iso-propyl amine (b.p. 116-118°C/760 mmHg), dibenzyl amine (b.p. 300°C/760 mmHg), piperidine (b.p. 106°C/760 mmHg), 2-ethyl piperidine (b.p. 143°C/760 mmHg), dicyclohexylamine (b.p. 113-115°C/760 mmHg), N-methyl cyclohexylamine (149°C/760 mmHg), 1,2,3,4-tetrahydroisoquinoline (b.p. 232-233°C/760 mmHg). 1,2,3,4-tetrahydroquinoline was prepared by a catalytic hydrogenation of quinoline²¹. The pure compound was obtained by column chromatography of the crude product on silica gel. Known methods were used to prepare 1,1-diphenylethylene²², methyl and ethyl α -cyano- β,β -diphenylacrylates²³ (A and A'), and cyanoacetic acid-9H-fluorene-9-ylidene ethyl ester²³ (B). Solutions of each of the different RMgBr used, in diethyl ether and in THF, were prepared by reacting the corresponding alkyl bromide with magnesium turnings, under nitrogen and anhydrous conditions. A 1.6 M solution of BuLi in hexane (Aldrich) was used. Solutions of each of the lithium amides $(R^1R^2CH)_2NLi^+$ used, were prepared by the addition of an equimolar amount of n-BuLi into a solution of the corresponding secondary amine in the required ethereal solvent, at -78°C.

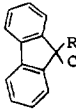
Solutions of known concentrations of all the reactants used, in diethyl ether and in THF, were kept in flasks fitted with self-sealing rubber septums. Required amounts of these solutions were added into the reaction flask with a hypodermic syringe. All manipulations and reactions were carried out under an atmosphere of dry nitrogen.

General Procedure for Reactions of Organometallic compounds with the Activated Olefins (A) and (B). - The reaction set-up consisted of a three-neck flask fitted with self-sealing rubber septum, equipped with magnetic stirring and a nitrogen inlet. All glass parts, syringes and needles were thoroughly dried at 120°C, assembled while warm. The ethereal solvent was distilled into the flask and the required amounts of solutions of n-BuLi or RMgBr were added to it. The ethereal solvent was cooled (0°C - -78°C) prior to the addition of the n-BuLi solution. The $(R^1R^2CH)_2NLi^+$ was prepared in the ethereal solvent at -78°C, by reacting equimolar amounts of n-BuLi and $(R^1R^2CH)_2NH$. The required amount of the activated olefin dissolved in the corresponding ether was added to the solution of the organic anion salt. Stirring of the reaction mixture was continued at room temperature for 2 hr (unless otherwise specified). The reaction mixture was then quenched by an aqueous solution of ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over anhydrous magnesium sulfate. ¹H-NMR spectrum of the recovered crude mixture of the reaction products was measured, in order to determine the extent of each of the hydride-transfer reaction, and of the Michael addition reaction. The relative amounts and the yields of the corresponding derivatives of either olefins (A), (A'), and (B) were determined by comparing the integration values of the absorptions at their characteristic chemical shifts.

Crude mixtures of reaction products obtained in many of the experiments were also subjected to column chromatography on silica gel. ¹H-NMR data of the separated Michael addition products and of the reduced derivatives of olefins (A), (A') and (B) are given in Table 6.

Preparation (in situ) of 1,1-diphenyl-1-lithio-hexane and its reaction with an H⁻-acceptor. The reaction set-up described above was used. The ethereal solvent (40 ml) was introduced, followed by

Table 6. ¹H-NMR Data of the Reaction Products Derived from Olefins (A), (A') and (B)

Compound		¹ H-NMR Data*
Ph ₂ C(R)-CH(CN)CO ₂ Me	R = H (AH ₂)	δ7.1-7.4 (m, 10H); 4.75 (d, J=8.4, 1H); 3.67 (s, 3H).
Ph ₂ C(Et)-CH(CN)CO ₂ Me	R = Et (EtAH)	δ7-7.2 (m, 10H); 4.34 (s, 1H); 3.56 (s, 3H); 2.20 (t, 2H); 1.2-1.6 (m, 4H); 0.73 (t, 3H).
Ph ₂ C(i-Bu)-CH(CN)CO ₂ Me	R = i-Bu (i-BuAH)	δ7.1-7.4 (m, 10H); 4.41 (s, 1H); 3.32 (s, 3H); 2.23 (dd, J=4.8, 1.0, 2H); 1.46 (m, 1H); 0.56 (d, J=6.7, 3H); 0.47 (d, J=6.6, 3H).
Ph ₂ C(n-C ₁₂ H ₂₅)-CH-CN CO ₂ Me	R = n-dodecyl (n-dodecyl-AH)	δ7.1-7.5 (m, 10H); 4.45 (s, 1H); 3.43 (s, 3H); 2.31 (t, J=8.0, 2H); 1.13 (m, 20H); 0.80 (t, J=6.3, 3H).
Ph ₂ C[(CH ₂) ₃ Ph]-CH-CN CO ₂ Et	R=Ph(CH ₂) ₃ (Ph(CH ₂) ₃ A'H)	δ7.0-7.5 (m, 15H); 4.42 (s, 1H); 3.38 (s, 3H); 2.53 (t, J=8.0, 2H); 2.30 (t, J=8.0, 2H); 1.40 (m, 2H).
 R CH(CN)CO ₂ Et	R = H (BH ₂)	δ7.1-7.7 (m, 8H); 4.54 (d, J=4.5, 1H); 4.21 (q, J=7.0, 2H); 4.10 (d, J=4.5, 1H) 1.17 (t, J=7.1, 3H).
	R = n-Bu (n-BuBH)	δ7.1-7.8 (m, 8H); 3.97 (s, 1H); 3.73 (dq, J=7.1, 1.4, 2H); 2.40 (ddd, J=13.2, 8.2, 8.2, 1H); 2.15 (ddd, J=13.2, 8.0, 8.0, 1H); 1.20 (m, 4H); 0.70 (t, 3H); 0.60 (t, 3H).
	R = i-Bu (i-BuBH)	δ7.5-7.7 (m, 3H); 7.1-7.4 (m, 5H); 3.87 (s, 1H); 3.65 (dq, J=7.1, 1.5, 2H); 2.47 (dd, J=13.7, 6.1, 1H); 2.11 (dd, J=13.7, 5.7, 1H); 0.87 (m, 1H); 0.67 (t, J=7.1, 3H); 0.39 (d, J=7.2, 3H); 0.35 (d, J=7.2, 3H).
	R = (CH ₂) ₃ Ph [Ph(CH ₂) ₃ BH]	δ6.8-7.8 (m, 13H); 3.95 (s, 1H); 3.69 (dq, J=7.1, 1.2, 2H); 2.56 (t, J=7.4, 2H); 2.39 (t, J=7.4, 2H); 1.33 (m, 2H); 0.70 (t, J=7.1, 3H).

* ¹H NMR spectra were recorded in CDCl₃ with a Bruker 200MHz NMR spectrometer with tetramethylsilane as an internal standard; δ and J values are in ppm and Hz, respectively.

the required amount of 1,1-diphenyl ethylene. The mixture was cooled to -78° in case of THF or - to 0°C in case of DEE. An equimolar amount of n-BuLi (hexane solution) was added, and the mixture was stirred for 20 min (THF, -78°C) or - for 60 min (DEE, 0°C). The reaction temperature was then adjusted to the required one, and ethyl α-cyano-β,β-diphenyl acrylate (A') was added. Stirring was continued for the required reaction period. Workup of the reaction mixture was carried out as described above. The crude mixture of products obtained was subjected to column chromatography (silica gel) and the yield of each product determined. The products isolated were: 1,1-diphenyl-hex-1-ene, 1,1-diphenyl hexane, the reduced (A) - Ph₂CH-CH(CN)CO₂Et (A'H₂) and the Michael addition product Ph₂C(n-Bu)-CH(CN)CO₂Et (n-BuAH). Unreacted 1,1-diphenylethylene and olefin (A') were isolated too.

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