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ARE DIFFERENT LITHIUM CARBENOIDS RESPONSIBLE FOR HOMOLOGATION AND METHYLENATION ?

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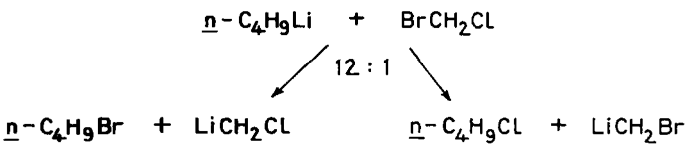
After reacting methyllithium with dibromomethane in ether, Kirmse and v. Wedel (1) obtained ethyl bromide (48%) and propyl bromide (13%). Even under conditions which we have described as optimal for the conversion of alkenes to cyclopropanes (2), the formation of homologous alkyl bromides remained the major reaction pathway. We wish to report that the homologous series from butyl to octyl bromide has been detected by capillary vpc analysis in the products from n-butyllithium and dibromo- or bromochloromethane in hexane. The first and third figure columns of Table I list the yields in mol% based on butyllithium. Since the formation of e.g. hexyl bromide requires 2 equivalents of $LiCH_2Hal$, the yields of the second and fourth column have been based on the generated lithium carbenoid.

Table I. Reactions of 11 mmol n-Butyllithium (free of LiHal) with 20 mmol CH_2BrX and 20 mmol Cyclohexene in 20 ccm Hexane at 0°

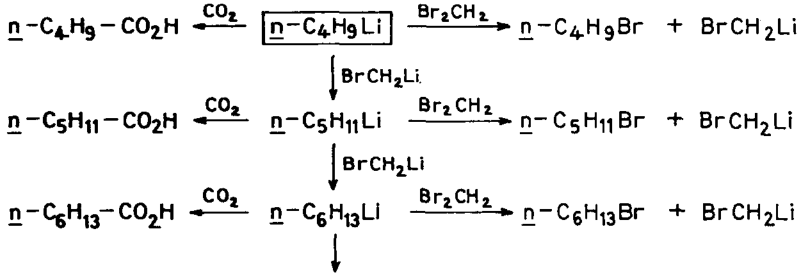
Product	X = Br		X = Cl	
	%(Butyl)	%($LiCH_2Br$)	%(Butyl)	%($LiCH_2Cl$)
n-Butyl bromide	46	-	53	-
n-Pentyl bromide	28	28	28	28
n-Hexyl bromide	12	24	9.7	20
n-Heptyl bromide	4.4	13	2.8	8.5
n-Octyl bromide	1.4	5.4	0.7	2.9
Norcarane		12.8		27
Ethylene		0.9		0.5

The gas chromatogram of the products from bromochloromethane disclosed small amounts of alkyl chlorides besides the alkyl bromides (in % of $LiCH_2Hal$): $C_5H_{11}Cl$ 2.2, $C_6H_{13}Cl$ 1.7, $C_7H_{15}Cl$ 0.8. Thus, the halogen-lithium interconversion seems to involve both halogen atoms.

On interrupting the reaction of dibromomethane with butyllithium by carboxylation at -100°, the capillary chromatogram reveals, after esterification with diazomethane, the homologous $CH_3(CH_2)_nCO_2CH_3$ (in % of butyllithium): n=3 16.2,



n=4 5.9, n=5 2.0, n=6 0.6. This indicates that not the alkyl halide, but rather the butyllithium undergoes the homologation. An analogous experiment with bromochloromethane furnished besides the aforementioned carboxylic esters, methyl chloroacetate (0.1%), which stems from the carboxylation of the short-lived species $LiCH_2Cl$ (4).



The homologation follows the scheme above in which the lithium carbenoid undergoes a step-wise insertion into alkyllithium - similar to a Wurtz type synthesis:

$$\underline{n}\text{-}C_4H_9Li + Br\text{-}CH_2Li \longrightarrow \underline{n}\text{-}C_5H_{11}Li + LiBr$$

The homologous lithium alkyls are converted to alkyl bromides by bromine-lithium exchange with CH_2BrX. On the assumption that the homologation of alkyllithium is much faster than the bromine-lithium exchange, then one half of RLi should be converted to RCH_2Li. The alkyl bromide yields listed in Table I are in fair accordance with the calculated power series.

A homologation of alkyllithium was discovered by Ziegler and Gellert (5). On treating dimethyl ether with butyllithium at 40°, the n-alkanes from butane to octane were isolated in decreasing amounts in addition to lithium methoxide.

The systems n-butyllithium + diiodomethane and tert.-butyllithium + dibromomethane have been studied as further examples of the homologation reaction. In the first case, the alkyl iodides from butyl to octyl iodide were analysed, while in the second reaction tert.-butyl, neopentyl and 3.3-dimethylbutyl bromide were isolated by preparative vpc and structurally confirmed by NMR.

Are methylenation of alkenes and homologation of lithium alkyls competing pathways of lithium carbenoids? The conversion yields of cyclohexene to norcarane decrease from 27 to 0.4% in going from $LiCH_2Cl$ to $LiCH_2I$ (2), whereas invariably ca. 70% of the lithium carbenoid enters into the homologation pathway. The surprising result of a variation of the mode of addition (Table II): The yields of norcarane and of homologous alkyl bromides remained constant within narrow limits and were independent of the stationary concentration of alkyllithium !

Table II. Variation of the Mode of Addition in the Reaction of 11 mmol n-C_4H_9Li + 30 mmol $BrClCH_2$ + 20 mmol Cyclohexene in 20 ccm Hexane at -50°; Yield Based on $LiCH_2Cl$.

Added	in Min.	Methylenation % Norcarane	Homologation % Alkyl Bromides
$BrClCH_2$	10	32	63
n-C_4H_9Li	10	32	62
n-C_4H_9Li	30	33	61
n-C_4H_9Li	60	33	58

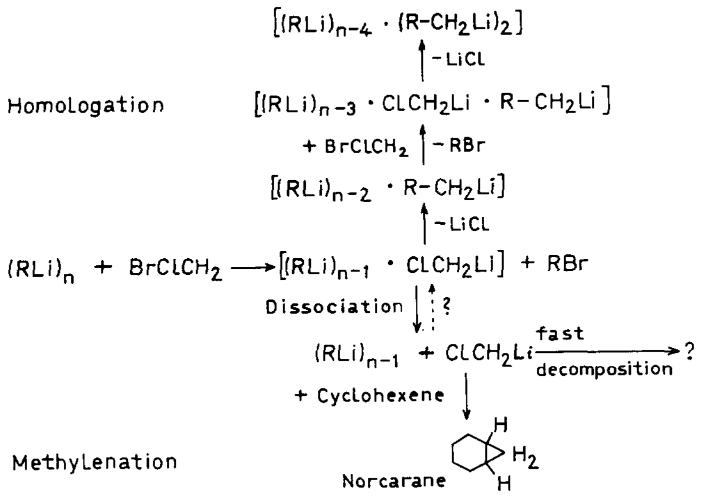
In the experiments of Table III n-butyllithium was introduced under standard conditions and the amount of cyclohexene was increased from 0 to 41 mmol. The norcarane yield was increased from 0 to 39% without a corresponding decrease in the homologation yield (ratio of alkyl bromides unchanged). The formation and consumption of the lithium carbenoid are fast reactions. For example, upon adding cyclohexene 1 min. later to the reaction mixture of $BrCH_2Cl$ + n-C_4H_9Li in hexane at -50°, only a trace of norcarane was formed.

Table III. Variation of Cyclohexene Concentration in the Reaction of 11 mmol n-C_4H_9Li (Added in 10 min.) with 20 mmol $BrClCH_2$ in 20 ccm Hexane at -50°; Yields Based on % $LiCH_2Cl$.

mMol Cyclohexene	% Methylenation	% Homologation
0	0	59
4	15	60
21	34	58
41	39	53

One gains the impression that the yields of the two reactions are predestined. Two different carbenoid species must be involved which are kinetically independent of each other.

One of the few reaction schemes which harmonizes with this conclusion is depicted below. Lithium alkyls are known to be associated in solution; n-C_4H_9Li is hexameric, tert.-C_4H_9Li tetrameric in cyclohexane (6). If we assume that the associated alkyllithium undergoes the halogen-lithium interconversion with the dihalomethane, then the halomethyllithium becomes part of the metalorganic aggregate. Within this aggregate the step-wise homologation is effected. It is



only after the halomethyllithium dissociates out of the aggregate that the now less stabilized *monomeric* LiCH$_2$Hal is capable of transforming alkenes into cyclopropanes. Is it not in contradiction with this scheme that the experimental facts require a nearly irreversible dissociation? A very short life-time of the monomeric lithium carbenoid would suppress its return to the aggregate. If the monomeric LiCH$_2$Hal does not find an alkene molecule, it most likely suffers fast and still unknown decompositions.

References

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