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COMPETITION OF ALKENES FOR METAL CARBENOIDS

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Relative reactivities of alkenes toward dihalocarbene have been measured (1); however not much is known of activity sequences versus CH_2 of halomethyl metals.

Chloromethyllithium was generated *in situ* from bromochloromethane with butyllithium in pentane solution of the competing olefins at -50°. After capillary vpc analysis of the cyclopropanes, the competition constants were calculated according to the equation (2):

$$\varkappa = \frac{k_A}{k_B} = \frac{\log A_o - \log (A_o - \text{A-adduct})}{\log B_o - \log (B_o - \text{B-adduct})}$$

The validity of the competition principle (parallel reactions of 2nd order) was established by 4 experiments in which the ratio styrene : cyclohexene was varied from 0.44 to 2.1 (3). The relative rate constants of Table I are based on k(cyclohexene) = 1.0. Experiments with *n*-butyl- and *tert*.-butyllithium furnished identical competition constants; the alkyllithium is only involved in the generation of $LiCH_2Cl$. However, bromomethyllithium prepared from CH_2Br_2 and $n\text{-}C_4H_9Li$ turned out to be somewhat more selective than chloromethyllithium (3).

Table I. Relative Methylenation Rates of Alkenes with Metal Carbenoids in Pentane at -50°. A. $BrClCH_2 + n\text{-}C_4H_9Li$ in the Presence of Pairs of Olefins (0.1 - 6.4 *m*); B. Carbenoid from $C_2H_5AlCl_2$ + Diazomethane with Pairs of Olefins (0.5 - 0.8 *m*).

Alkene	k_{rel} $LiCH_2Cl$	k_{rel} $C_2H_5Al(CH_2Cl)Cl$
Tetramethylethylene	0.28, 0.30	0.01
1-Methylcyclohexene	0.68, 0.68[a]	0.47
Cyclohexene	1.00	1.00
Norbornene	1.09, 1.11	0.65
1-Octene	1.25, 1.21	0.14, 0.13, 0.14
α-Methylstyrene	3.5	
Styrene	3.7, 4.0, 3.6, 3.6	
Styrene[b]	5.6, 5.3, 5.5, 5.3	
Cyclopentene		0.81, 0.80

[a] *tert*.Butyllithium instead of $n\text{-}C_4H_9Li$; [b] k_{rel} $LiCH_2Br$.

The k_{rel} values of Table I stretch over a bit more than one power of ten. This would appear to be a small effect when compared with the six magnitudes of bromination rate constants between ethylene and its tetramethyl derivate (4). However, the spread is large if one contrasts the metal carbenoid with the unselective free CH_2 (1).

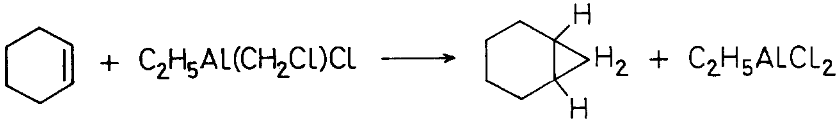
3.4-Dihydro-2H-pyran is not converted to a cyclopropane derivative by $LiCH_2Cl$; also the methylenation of cyclohexene is blocked in the presence of this cyclic vinyl ether. The coordination with the ether oxygen atom deprives $LiCH_2Cl$ of its capacity for CH_2-transfer.

In contrast to the short-lived species $LiCH_2Hal$ (5), the <u>in situ</u>-preparation of aluminium carbenoids is dispensible; Hoberg (6) obtained crystalline iodomethyl-diethyl-aluminium at -80°. Methylenations with this reagent were effected in a temperature region below that of self-decomposition (6).

We reacted 1.8 mmol ethylaluminium dichloride (1) and 50 mmol cyclohexene with 11.4 mmol diazomethane in pentane at -50° and obtained 6.2 mmol norcarane (2). This is 3.6 times the amount of 1 which acts as a catalyst. It is an open question whether the mono- or bis-chloromethyl compound of aluminium is involved.

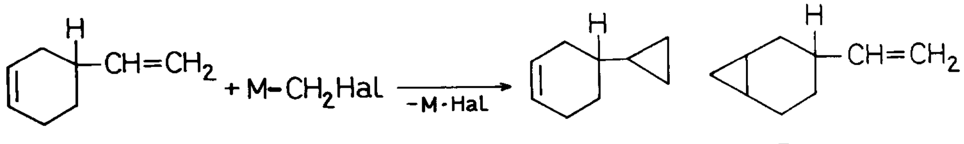
$$C_2H_5AlCl_2 + CH_2N_2 \longrightarrow C_2H_5Al(CH_2Cl)Cl + N_2$$

1



2

With the same aluminium carbenoid we have carried out competition methylenations with pairs of olefins (Tabele I). Three experiments with variation of the ratio 1-octene : cyclohexene from 0.22 to 3.2 provided the same competition constant. This carbenoid initiated polymerisation of styrene and α-methylstyrene. A striking difference in the activity sequences of alkenes towards lithium and aluminium carbenoids is encountered in the k_{rel} of a monosubstituted ethylene (1-octene) which are different by a factor of 11. The aluminium carbenoid displays a rate maximum with the 1.2-disubstituted ethylene (cyclohexene).



3 4 5

The two double bonds of 4-vinylcyclohexene (3) offer an intramelecular competition system for metal carbenoids. By preparative vpc the cyclopropanes 4 and 5 were separated. The NMR spectra confirmed the structural assignment which had been proposed on the base of the IR-spectrum of a mixture 4 + 5 (7). While lithium carbenoids furnished values near 1.1 for k(4)/k(5), a decrease by a factor of 10 towards the aluminium carbenoid is observed. Zinc carbenoids are of intermediate selectivity.

Table II. Intramolecular Competition of the Vinyl Group and the Endocyclic Double Bond of 4-Vinylcyclohexene for Metal Carbenoids

Carbenoid Generator	Solvent, Temperature	k(4)/k(5)
n-C_4H_9Li + $BrClCH_2$	Pentane, -50°	1.15
tert.-C_4H_9Li + $BrClCH_2$	"	1.14
tert.-C_4H_9Li + Br_2CH_2	"	1.11
tert.-C_4H_9Li + I_2CH_2	"	1.10
$C_2H_5AlCl_2$ + CH_2N_2	"	0.11
Zn/Cu + I_2CH_2	Ether, 35°	0.51, 0.49, 0.50
ZnI_2 + CH_2N_2	"	0.51, 0.50, 0.50
Zn/Cu + Br_2CH_2	"	0.46, 0.44, 0.45
$ZnBr_2$ + CH_2N_2	"	0.45, 0.44, 0.44

Simmons and Smith (8) have made zinc carbenoids readily available from diiodomethane and zinc-copper, whereas Wittig and Schwarzenbach (9) have employed zinc halide and diazomethane. Competition constants towards the reagent CH_2I_2 + Zn/Cu have already been measured (10, 11). Their independence of the total concentration of olefins (2.1 - 4.2 *m*) was demonstrated, but not the independence on the ratio of olefins.

Our competition experiments with zinc carbenoids encountered considerable difficulties. On decreasing the ratio 1-methylcyclopentene : cyclohexene from 1.4 to 0.34, the competition constant dropped from 4.9 to 2.8, i.e. it was not a constant value any more. The pair 3.4-dihydro-2H-pyran / cyclohexene showed a fair constancy of k_{rel} for diiodomethane + zinc/copper, whereas the ratio zinc iodide : diazomethane strongly influenced k_{rel} (Table III). It is only with some reservations that we conclude from our experiments that one and the same carbenoid - either iodomethylzinc iodide or bis-iodomethylzinc - occurs in both reagents, methylene iodide + zinc/copper as well as zinc iodide + diazomethane. We conjecture that the zinc carbenoids are not homogenous.

The intramolecular competition constants for 4-vinyl-cyclohexene are better reproducible (Table II). The evidence for a common zinc warbenoid inter-

Table III. Competition of 3.4- Dihydro-2H-pyran and Cyclohexene for Zinc Carbenoid in Boiling Ether. Generator: A. Zinc/Copper + Diiodomethane; B. Zinc Iodide + Diazomethan. Analysis: Zn by Complexometry, Carbenoid-CH_2 by Iodometry.

	3.4-Dihydropyran m	Cyclohexene m	Min.	k_{rel}	Ratio Zn : (CH_2)
A.	0.15	1.32	20	7.3	
	0.15	1.32	30	7.4	
	0.76	0.68	270	7.5	
	0.76	0.68	300	7.7	
B.	0.34	2.12	10	6.9	0.70
	0.34	2.12	40	7.6	0.70
	0.27	1.69	40	8.7	0.76
	0.27	1.69	40	9.7	1.1

mediate is only restricted by the close to 1.0 values for k(**4**)/k(**5**). The data of Table II suggest that selective methylenations of polyunsaturated compounds are feasible.

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