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STEREOSPECIFIC ADDITION REACTION BETWEEN BUTADIENE AND AMINES

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The alkali metal initiated addition of amines to conjugated dienes have been reported recently.1)-3) This communication is concerned with studies on the unique aspects of the stereospecific addition reaction between butadiene and diethyl-, diisopropyl- and diisobutylamine.

A stereospecific addition reaction has been found between butadiene and secondary amines. For instance, 1-diethylamino-cis-butene-2 was formed from Et_2NH in high yield according to Eqs. (1), (2) and (3).

$$Et_2NH + n\text{-}BuLi \xrightarrow[C_6H_{12}]{} Et_2NLi + n\text{-}BuH \qquad (1)$$

$$Et_2NLi + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[C_6H_{12}]{(Et_2NH)} Et_2NC_4H_6Li \qquad (2)$$

(recycle)

$$Et_2NC_4H_6Li + Et_2NH \xrightarrow[C_6H_{12}]{} \underset{\text{(cis 98 - 99 \%)}}{Et_2NCH_2{-}CH{=}CH{-}CH_3} + Et_2NLi \qquad (3)$$

Amino-hydrogen seemed to play an essential role in this stereospecific reaction, because the addition of lithium diethylamide to butadiene in cyclohexane (Eq. (2)) was found to fail in the absence of amino-hydrogen(N-H) in the reaction system. High concentration of the N-H species, however, caused a drastic decrease in the stereospecificity of the reaction. On the basis of spectroscopic and kinetic studies, a complex formed from Et_2NLi and Et_2NH in one to two mole ratio was suggested to be the chemical species responsible for the addition reaction (Eq. (2)).

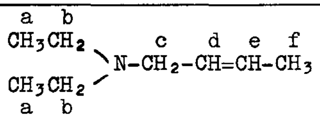
In order to investigate the metalation reaction of secondary amines(R_2NH) (Eq. (1)), a cyclohexane solution of n-BuLi was added by a syringe into the solution of R_2NH in cyclohexane under nitrogen at 0°C. After 5-minute stirring, an excess of CCl_4 was added, the reaction mixture was treated with water, and then n-butane present in the oil phase was analyzed by vapor phase chromatography (VPC). Since non-reacting n-BuLi remaining in the reaction system, if any, should have been decomposed by CCl_4, the observed n-butane in VPC had been formed in the metalation reaction before the addition CCl_4. It was confirmed from the results of measurement that the metalation reaction in the R_2NH-n-BuLi (R=Ethyl, Isopropyl, and Isobutyl) system proceeded stoichiometrically to form lithium dialkylamide(R_2NLi).

To the mixture of Et_2NLi and Et_2NH in cyclohexane, butadiene was added and stirred at 50°C for 60 min. The conversion of butadiene and the amounts of each product were determined by VPC. 1-Diethylamino-cis-butene-2 was formed with 98 - 99 % selectivity. The spectral data of products were shown in Table 1.

Table 1 Analysis of Products from Butadiene and Diethylamine

1-Diethylamino-butene-2*	MASS spectra m.w.	NMR spectra (τ value)					IR spectra characteristic absorption cm^{-1}
		a	b	c	d,e	f	
cis	127 (127.2)**	9.10 6H,t	7.65 4H,q	7.06 2H,d	4.63 2H,m	8.44 3H,d	690 δ CH(cis-CH=CH-)
trans	127 (127.2)**	9.10 6H,t	7.66 4H,q	7.13 2H,d	4.62 2H,m	8.39 3H,d	969 δ CH(trans-CH=CH-)

*

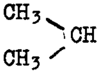
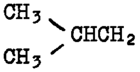


$$(\overset{a}{CH_3}\overset{b}{CH_2})_2N-\overset{c}{CH_2}-\overset{d}{CH}=\overset{e}{CH}-\overset{f}{CH_3}$$

** Values in parentheses are the calculated ones.

Other dialkylamines were allowed to react with butadiene under the same conditions. .Results obtained are shown in Table 2.

Table 2 Stereospecific Butenylation of R_2NH*

R	$\frac{[R_2NH]_0}{[R_2NLi]_0}$	Products % on butadiene	Microstructures of products		
			vinyl %	trans %	cis %
CH_3CH_2	0	0	—	—	—
	3	50	0	2	98
$CH_3CH_2CH_2$	3	47	0	7	93
$CH_3CH_2CH_2CH_2$	3	29	0	5	95
 $(CH_3)_2CH$	3	0	—	—	—
 $(CH_3)_2CHCH_2$	0	0	—	—	—
	3	87	0	20	80

* $[R_2NLi]_0$ 0.25 mol/l [butadiene]$_0$ 0.25 mol/l

Solvent; cyclohexane, Reaction temperature; 50°C, Reaction time; 60 min.

1-Di-n-alkylamino-cis-butene-2 (n-R=Ethyl, n-Propyl, and n-Butyl) was formed in higher selectivity than 1-diisobutylamino-cis-butene-2. Diisopropylamine did not give addition products.

Table 2 also indicated that no addition took place in the absence of N-H species. No addition product was detected with VPC even in such a polar solvent as triethylamine or tetramethylethylenediamine, which are known to form a complex with organolithium compounds. This result suggests different role of the amino-hydrogen in the addition reaction other than that of the polar solvents.

In order to clarify the nature of the chemical species present in the R_2NLi-R_2NH system, the infrared spectra were measured on changing the ratio (R_2NLi/R_2NH) and the concentration of the two components. The absorbance at 650 cm^{-1}, assignable to be characteristic for free N-Li, was observed to decrease as the ratio of the total concentration of N-H increased against N-Li. With the aid of a calibration curve for the free N-Li species, the ratio of NH complexed with NLi was calculated as shown in Table 3.

Table 3 Analysis of $(Isobutyl)_2NLi$-$(Isobutyl)_2NH$ System* with Infrared Spectra

Total concentration			$[NLi]_{free}$	$[NLi]_{complexed}$	$\frac{[NH]}{[NLi]}$ in complex
$[NH]_0$ mol/l	$[NLi]_0$ mol/l	$\frac{[NH]_0}{[NLi]_0}$			
0	0.20	0	0.20	0	—
0.10	0.20	0.5	0.15	0.05	2.0
0.20	0.20	1.0	0.095	0.105	1.9
0.40	0.20	2.0	0.0	0.20	2.0

* Solvent cyclohexane

It is seen from Table 3 that R_2NLi and R_2NH form a complex [A] in one to two mole ratio.

Kinetic studies revealed that the rate (v) of the addition reaction was expressed as Eq. (4):

$$v = k'[\text{Butadiene}] \qquad (4)$$

Furthermore, the rate constant, k', was found to be in first order dependence upon the concentration of the one to two complex [A] as shown in Eq. (5):

$$k' = k[A] \qquad (5)$$

Any calculated values for the rate constant, k, were in excellent agreement with one another. For instance, k (in cyclohexane at 50°C); 8.5×10^{-4} (l/mol. sec) for diethylamine; 2.4×10^{-3} (l/mol. sec) for diisobutylamine.

In conclusion, this addition reaction between amines and butadiene seems to proceed via complex formation of R_2NLi with R_2NH in one to two mole ratio, producing 1-dialkylamino-cis-butene-2 in a stereospecific fashion. Full details on the kinetic and spectroscopic studies will be reported in near future.

References

1) O. Schmidt, F. A. Fries, and L. Kollek, German Patent, 528,466 (1931)

2) E. A. Zuech, R. F. Kleinschmidt, and J. E. Mahan, J. Org. Chem., **31**, 3713 (1966)

3) G. T. Martirosyan, E. A. Grigoryan, and A. T. Babayan, Arm. Khim. Zh., **20** (6) 423 (1967); C. A., **68**, 48940 (1968)