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Stereospecific Addition Reaction between Butadiene and Amines

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The reaction of butadiene with secondary amines initiated by *n*-butyllithium was found to proceed selectively to produce 1-dialkylamino-*cis*-butene-2 under appropriate reaction conditions. For instance, diethylamine produced 1-diethylamino-*cis*-butene-2 in a 98—99% purity. By kinetic and spectroscopic studies, it was concluded that the lithium dialkylamide–dialkylamine (1:2) complex plays an important role in this addition reaction. The second-order rate constants of the reaction are 0.85×10^{-3} l/mol sec for diethylamine and 2.4×10^{-3} l/mol sec for diisobutylamine.

It was previously reported that the reactivity of lithium alkyl was drastically influenced by coupling with lithium 2-alkoxyethoxide.[1–5] Since it seemed worthwhile to examine the influence of lithium 2-alkoxyethoxide upon the reactivity of lithium amide, reactions between butadiene and lithium dialkylamides were studied in the presence of the 2-alkoxyethoxide. Contrary to the case of lithium alkyl, the reactivity of the lithium amide was not significantly influenced by the 2-alkoxyethoxide. However, it was unexpectedly found that lithium dialkylamide was activated in a specific fashion by the stoichiometric quantity of the parent dialkylamine.

This paper will present the results of a study of the reaction of butadiene and dialkylamine initiated by *n*-butyllithium and producing 1-dialkylaminobutene derivatives. A preliminary report of the results was published elsewhere.[6]

Experimental

Most of the experiments were carried out under purified nitrogen to preclude oxygen and atmospheric moisture.

Reagents. Cyclohexane, butadiene, and amines were purified by the usual method. *n*-Butyllithium was prepared from *n*-butyl chloride and lithium metal in purified petroleum ether and was used as a cyclohexane solution.

Synthesis of 1-Dialkylaminobutene Derivatives. The addi-

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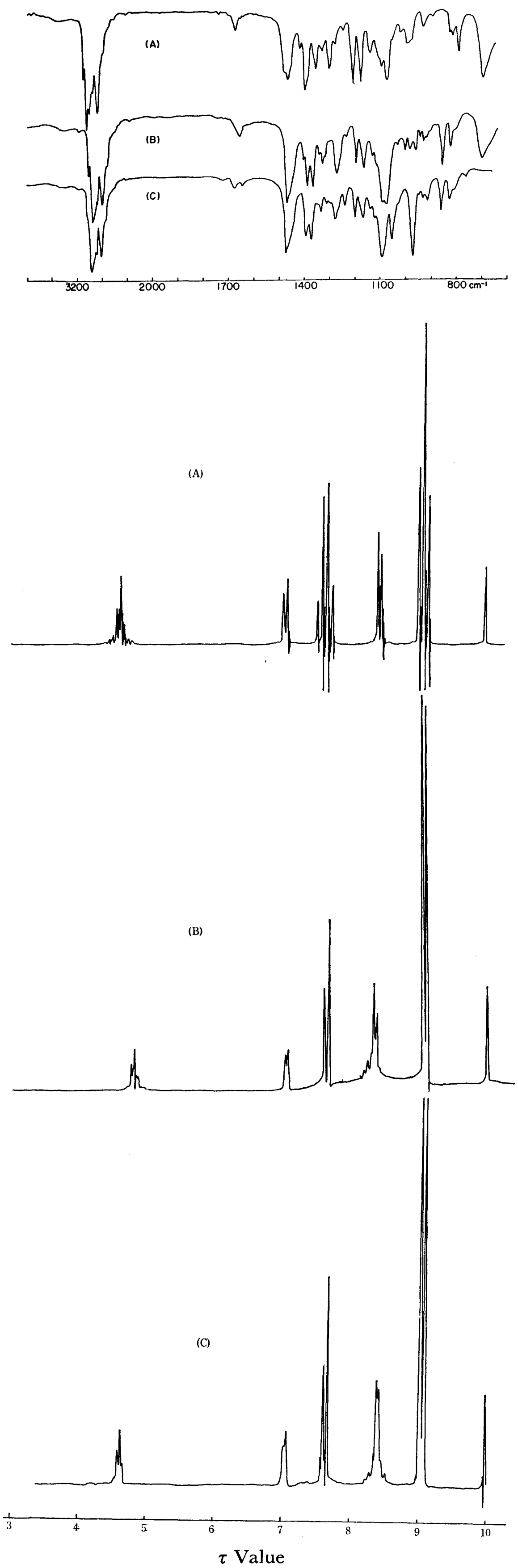


Fig. 1. IR and NMR spectra of (A) 1-diethylamino-*cis*-butene-2, (B) 1-diisobutylamino-*cis*-butene-2, and (C) 1-diisobutylamino-*trans*-butene-2.

tion products of dialkylamine to butadiene were isolated as follows. A 200 ml flask was equipped with a reflux condenser with a dry ice–methanol refrigerant and a KOH drying column. A 100 mmol portion of butadiene vapor was introduced through the KOH column for two hours into a magnetically-stirred cyclohexane solution at 50 °C, into which dialkylamine (100 mmol) and *n*-butyllithium (5 mmol) were added. After the mixture has been stirred another three hours at 50°C, the reaction was stopped by the addition of a small amount of methanol. The products were isolated by fractional distillation and by preparative vapor phase chromatography (vpc). The analyses of the products were performed by NMR, IR, and mass spectrometry. The analytical data are shown in Table 1 and Fig. 1.

Metalation of Amines. A cyclohexane solution of *n*-butyllithium was added to a solution of secondary amine at 0 °C by means of a syringe. After five minutes stirring, an excess of carbon tetrachloride was added in order to decompose the residual *n*-butyllithium; then the mixture was treated with water. *n*-Butane present in the oil layer was analyzed by vpc.

Kinetics of the Addition Reaction. Into a round-bottomed flask equipped with a three-way stop cock, butadiene and cyclohexane were introduced. A solution of the lithium dialkylamide-dialkylamine complex was then added into the flask. The reaction was quenched after various time intervals by sampling a portion of the solution and adding it to an ether solution of methanol. The products were analyzed by vpc.

Results and Discussion

Synthesis of 1-Dialkylaminobutene Derivatives. The results of the addition reaction of dialkylamines to butadiene initiated by a catalytic amount of *n*-butyllithium are summarized in Table 2. The yields of the butenylation products were all about 85% except for the case of diisopropylamine. Higher-molecular-weight compounds than the simple butenylation products were not detected by vpc under these reaction conditions.

Kinetic Studies of the Addition Reaction. The addition reaction of dialkylamine to butadiene in the presence of *n*-butyllithium was assumed to proceed through the following three steps:

$$R_2NH + n\text{-}C_4H_9Li \longrightarrow R_2NLi + n\text{-}C_4H_{10} \tag{1}$$

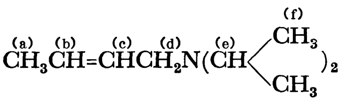
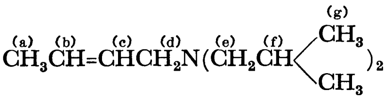
$$R_2NLi + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{k_b} R_2NC_4H_6Li \tag{2}$$

$$R_2NC_4H_6Li + R_2NH \xrightarrow{k_t} R_2NC_4H_7 + R_2NLi \tag{3}$$

At first, the metalation of dialkylamine with *n*-butyllithium, Eq. (1), was examined in cyclohexane. After the dialkylamine had been reacted with *n*-butyllithium, the cyclohexane solution was treated with carbon tetrachloride and then with water. The mol of *n*-butane recovered by vpc should be equal to that of the lithium amide formed, since the non-reacting *n*-butyllithium should have been decomposed by CCl_4. The results shown in Table 3 clearly indicate that the reaction of dialkylamine and *n*-butyllithium proceeds stoichiometrically at 0 °C within 5 min to produce lithium dialkylamide.

The dependence of the butadiene concentration on

Table 1. Analysis of products from dialkylamine and butadiene

Reaction products		NMR spectra (τ value) (a)	(b)(c)	(d)	(e)	(f)	(g)	(h)	Mass spectra M.W.[a]	IR spectra characteristic absorption cm^{-1}
$\overset{(a)}{CH_3}\overset{(b)}{CH}=\overset{(c)}{CH}\overset{(d)}{CH_2}N(\overset{(e)}{CH_2}\overset{(f)}{CH_3})_2$	*cis*	8.44 3H, d	4.63 2H, m	7.06 2H, d	7.65 4H, q	9.10 6H, t			127 (127.2)	690 δCH(*cis*-CH=CH–)
	trans	8.39 3H, d	4.62 2H, m	7.13 2H, d	7.66 4H, q	9.10 6H, t			127 (127.2)	969 δCH(*trans*-CH=CH–)
$\overset{(a)}{CH_3}\overset{(b)}{CH}=\overset{(c)}{CH}\overset{(d)}{CH_2}N(\overset{(e)}{CH_2}\overset{(f)}{CH_2}\overset{(g)}{CH_3})_2$	*cis*	8.41 3H, d	4.50 2H, m	6.98 2H, d	7.71 4H, t	8.61 4H, m	9.09 6H, t		155 (155.3)	690 δCH(*cis*-CH=CH–)
$\overset{(a)}{CH_3}\overset{(b)}{CH}=\overset{(c)}{CH}\overset{(d)}{CH_2}N(\overset{(e)}{CH_2}\overset{(f)}{CH_2}\overset{(g)}{CH_2}\overset{(h)}{CH_3})_2$	*cis*	3H, d	2H, m	2H, d	4H, t	4H, m	4H, m	6H, t	183 (183.3)	690 δCH(*cis*-CH=CH–)
 $\overset{(a)}{CH_3}\overset{(b)}{CH}=\overset{(c)}{CH}\overset{(d)}{CH_2}N(\overset{(e)}{CH}(\overset{(f)}{CH_3})_2)_2$	*cis*	8.44 3H, d	4.71 2H, m	7.01 2H, d	7.07 2H, m	9.10 12H, d			155 (155.3)	690 δCH(*cis*-CH=CH–)
	trans	8.40 3H, d	4.65 2H, m	7.06 2H, d	7.05 2H, m	9.10 12H, d			155 (155.3)	969 δCH(*trans*-CH=CH–)
 $\overset{(a)}{CH_3}\overset{(b)}{CH}=\overset{(c)}{CH}\overset{(d)}{CH_2}N(\overset{(e)}{CH_2}\overset{(f)}{CH}(\overset{(g)}{CH_3})_2)_2$	*cis*	8.42 3H, d	4.52 2H, m	7.03 2H, d	7.98 4H, d	8.33 2H, m	9.08 12H, d		183 (183.3)	701 δCH(*cis*-CH=CH–)
	trans	8.33 3H, d	4.51 2H, m	7.09 2H, d	7.99 4H, d	8.33 2H, m	9.09 12H, d		183 (183.3)	968 δCH(*trans*-CH=CH–)

a) Values in parentheses are the calculated ones.

Table 2. Addition reaction products of dialkylamine with butadiene initiated by *n*-butyllithium[a]

Amine	Total yield (%)	Microstructures of products Vinyl (%)	*trans* (%)	*cis* (%)
Diethylamine	86	1	12	87
Di-*n*-propylamine	86	trace	12	87
Di-*n*-butylamine	75	0	14	86
Diisopropylamine	9	0	45	55
Diisobutylamine	84	0	22	78

a) Dialkylamine 100 mmol, butadiene 100 mmol, *n*-butyllithium 5 mmol, 50 °C.

Table 3. Reaction of dialkylamine with *n*-butyllithium[a]

Amine	Yield of lithium amide (%)
Diethylamine	103
Diisopropylamine	100
Diisobutylamine	99

a) Reaction temp.: 0 °C, reaction time: 5 min.

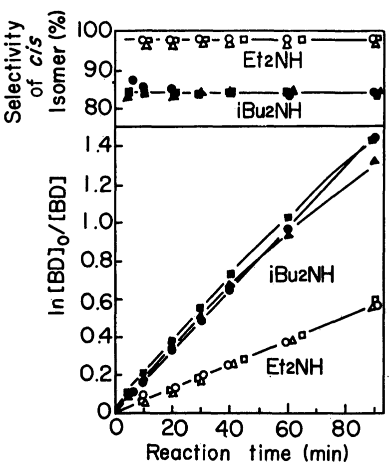


Fig. 2. Dependence of butadiene concentration on addition reaction rate.
$[Butadiene]_0/[R_2NLi]_0$ Value, ●○: 1.0, ■□: 2.0, ▲△: 3.0. $[R_2NH]_0=0.375$ M, $[R_2NLi]_0=0.125$ M. Solvent: cyclohexane, reaction temp.: 50 °C

the reaction rate was examined with the ratio of initial concentrations, $[R_2NH]_0$: $[R_2NLi]_0$, being three to one, where R were ethyl and isobutyl. The straight lines in Fig. 2 show that the reaction is in a first-order dependence on the butadiene concentration below the 60% conversion.

The rate, v, of the addition is expressed by Eq. (4):

$$v = k'[\text{butadiene}] \quad (4)$$

The relationship between k' and the initial concentration of lithium dialkylamide at the concentration of $[R_2NH]_0$: $[R_2NLi]_0=3$: 1 is shown in Fig. 3. Pseudo first-order rate constants, k', were found to be proportional to the concentration of lithium dialkylamide

$$k' = k[R_2NLi] \quad (5)$$

where k is the rate constant of the reaction.

The results presented above seem to mean that the rate of the addition reaction varies as the first-order of the concentrations of butadiene and lithium dialkylamide respectively. In the absence of dialkylamine, however, no addition reaction proceeded in cyclohexane, as is shown in Table 4. Addition products were not detected even in such polar solvents as triethylamine or *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, which are known to form associated complexes with organolithium compounds. These results suggest that the role of amino-hydrogen is different from that of the usual polar solvents.

In order to get some more information on the species, infrared spectroscopic analyses were carried out with

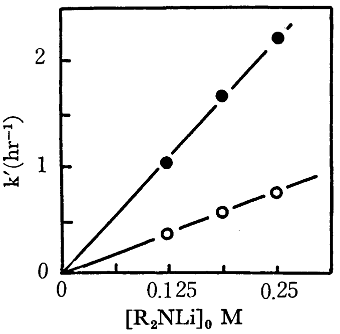


Fig. 3. Relationship between pseudofirst-order rate constant and [R_2NLi]. [R_2NH]$_0$/[R_2NLi]$_0$ = 3.0, [Butadiene]$_0$ = 0.250 M.
Solvent: cyclohexane, reaction temp.: 50 °C
●: diisobutylamine, ○: diethylamine

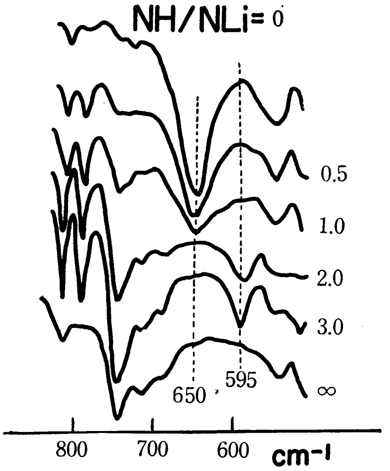


Fig. 4. (A) IR spectra of i-Bu_2NH—i-Bu_2NLi system. [i-Bu_2NLi] = 0.2 M, solvent: cyclohexane.

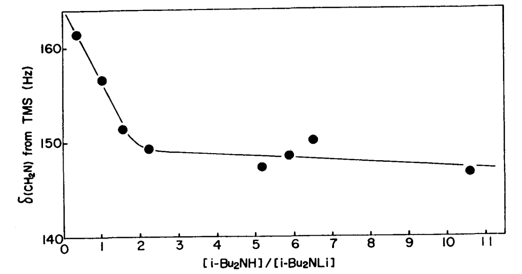


Fig. 4(B). Relation between NMR chemical shift of CH_2N and [i-Bu_2NH]/[i-Bu_2NLi] value.
[i-Bu_2NLi] = 1 M, solvent: benzene, 60 MHz

a mixture of lithium diisobutylamide and diisobutylamine. As is shown in Fig. 4(A), the absorption at 650 cm^{-1} was assignable to the free N–Li stretching frequency, because the characteristic absorptions of C–Li and O–Li were known to appear at 548 and 577 cm^{-1} respectively. The absorption at 650 cm^{-1} decreased as the ratio of the diisobutylamine concentration to the lithium diisobutylamide concentration increased. The absorption disappeared when the ratio exceeded 2.0. At [NH]/[NLi] = 2.0 and 3.0 a new peak was observed at 595 cm^{-1}; this peak was detected in the spectrum of neither diisobutylamine nor lithium diisobutylamide. Therefore, this new peak was assigned to a complex of lithium diisobutylamide with diisobutylamine. With the aid of the calibration curve, the concentration of the complex present in the system was calculated from the absorbance of the peak at 650 cm^{-1}. The complex formation of lithium dialkylamide-dialkylamine (1 : 2) can clearly be seen from the results shown in Table 5.

The formation of the one-to-two complex was also

TABLE 4. STEREOSPECIFIC BUTENYLATION OF R_2NH WITH BUTADIENE[a]

R	$\frac{[R_2NH]_0}{[R_2NLi]_0}$	Products yield (%) on butadiene	Microstructure 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
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH$	3	0	—	—	—
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH_2$	0	0	—	—	—
	3	87	0	20	80

a) [R_2NLi]$_0$ 0.25 mol/l. [Butadiene]$_0$ 0.25 mol/l.
Solvent: cyclohexane, reaction temperature: 50 °C, reaction time: 60 min.

TABLE 5. ANALYSIS OF (i-C_4H_9)$_2$ NLi–(i-C_4H_9)$_2$NH SYSTEM WITH INFRARED SPECTRA AT 650 cm^{-1} BAND[a]

Total concentration: [NH]$_0$ mol/l	[NLi]$_0$ mol/l	$\frac{[NH]_0}{[NLi]_0}$	[NLi]$_{free}$	[NLi]$_{complex}$	$\frac{[NH]}{[NLi]}$ in complex
0	0.20	0	0.20	0	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

a) Solvent: cyclohexane.

suggested by the NMR spectra shown in Fig. 4(B), in which an inflection point was observed at [NH]/[NLi]=2.0. As the proton-exchange reaction between *i*-Bu_2NH and *i*-Bu_2NLi is fast at room temperature, the methylene NMR signals of the complex are observed at the average value of the corresponding signals for its components. Furthermore, an exchange reaction should also be possible between the complex and free *i*-Bu_2NH when more than two times as much of the latter is present as *i*-Bu_2NLi. Another exchange reaction, on the other hand, is operative in the reaction between the complex and free *i*-Bu_2NLi in the region to the left of the inflection point in Fig. 4(B).

The overall scheme of the addition reaction may be drawn as follows:

$$R_2NLi + 2R_2NH \longrightarrow R_2NLi\cdot 2R_2NH \qquad (6)$$

$$R_2NLi\cdot 2R_2NH + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{k_b} R_2NC_4H_6Li\cdot 2R_2NH \qquad (7)$$

$$R_2NC_4H_6Li\cdot 2R_2NH + R_2NH \xrightarrow{k_t} R_2NCH_2CH{=}CHCH_3 + R_2NLi\cdot 2R_2NH \qquad (8)$$

Since the butenylation, Eq. (7), should be the rate-determining step of the addition reaction, the rate can be expressed as follows:

$$v = k_b[\text{complex}][\text{butadiene}] \qquad (9)$$

In the region of $[R_2NH]/[R_2NLi]>2$, the concentration of the complex is controlled by the concentration of lithium amide, so that Eq. (9) can be reduced to Eq. (10):

$$v = k_b[R_2NLi][\text{butadiene}] \qquad (10)$$

Equation (10) well explains the results of Fig. 2. On the contrary, in the region of $[R_2NH]/[R_2NLi]\leqq 2$, the concentration of the complex should be controlled by the concentration of dialkylamine, so that Eq. (9) can be reduced to Eq. (11):

$$v = \frac{1}{2}k_b[R_2NH][\text{butadiene}] \qquad (11)$$

As a matter of fact, Eq. (11) can be used in the analyses of the addition reaction in the region of $[R_2NH]/[R_2NLi]\leqq 2$, as is shown in Fig. 5.

The rate constants of the reactions calculated from Eq. (9) are summarized in Table 6.

Diisopropylamine did not react with butadiene. No infrared peak assignable to a complex of amine and lithium amide was observed. The steric hindrance of the isopropyl group is presumably the reason for the low reactivity of diisopropylamine.

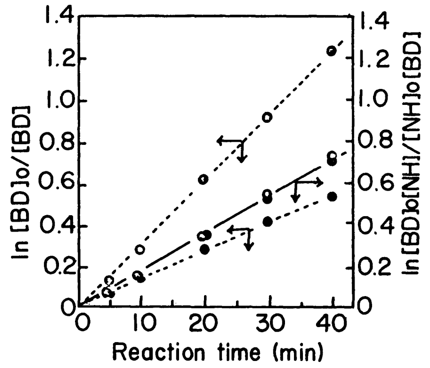


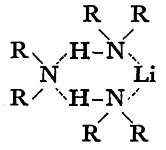
Fig. 5. First and second order analyses of the addition reaction of diisobutylamine with butadiene.
[*i*-$Bu_2NLi]_0$=[Butadiene]$_0$=0.25 M, solvent: cyclohexane, reaction temp. 50 °C.
[*i*-$Bu_2NH]_0$/[*i*-$Bu_2NLi]_0$ value ●: 1.0, ○: 2.0

TABLE 6. RATE CONSTANTS OF THE ADDITION REACTION OF $R_2NLi\cdot 2R_2NH$ WITH BUTADIENE

R	$k\times 10^3$ l/mol sec	*cis* Isomer content (%)	
		30 min	60 min
CH_3CH_2	0.85	99	99
$CH_3CH_2CH_2$	0.66	94	93
$CH_3CH_2CH_2CH_2$	0.41	96	95
$(CH_3)_2CH$	0	—	—
$(CH_3)_2CHCH_2$	2.4	80	80

The selectivity of the reaction to produce the *cis* isomer decreased when the $[R_2NH]/[R_2NLi]$ value increased (*cf.* Tables 2, 4, and Fig. 2). The selectivity is also affected by the structures of the alkyl groups of dialkylamine, as is shown in Tables 2 and 4. It can safely be concluded that di-*n*-alkylamine produces the *cis* isomer in high purity. Especially, diethylamine gives the *cis* isomer in a 98—99% purity.

Although the structure of the complex has not been clearly elucidated, we wish to propose the following structure on the basis of NMR, IR, and the reactivity of the complex:



This structure can probably explain the finding that *N*,*N*,*N′*,*N′*-tetramethylethylenediamine and triethylamine do not have any positive effects on the reaction of lithium dialkylamide.