

BUTYL LITHIUM-CATALYZED STEREOSELECTIVE TELOMERIZATION OF 1,3-DIENE  
- A NOVEL SYNTHESIS OF N,N-DIALKYL(OCTA-cis-2,6-DIENYL)AMINE DERIVATIVE -

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Palladium or nickel complex-catalyzed telomerizations of 1,3-dienes with active hydrogen compounds (carboxylic acids<sup>1</sup>), alcohols<sup>1</sup>), <sup>2</sup>), active methylene compounds<sup>3</sup>), water<sup>4</sup>) and amines<sup>5</sup>) have been reported to yield the corresponding octa-2,7-dienyl derivatives mainly.

We now report the n-butyl lithium-catalyzed telomerization of 1,3-diene with sec-amine<sup>6</sup>) as the novel synthetic method for N,N-dialkyl(octa-cis-2,6-dienyl)amine (Table 1.).

For example, an ether solution(6.5 ml) of n-butyl lithium(0.01 mol) was added to oxygen free benzene(20 ml) solution of buta-1,3-diene(12 ml, 0.15 mol) and diethylamine(3.65 g, 0.05 mol) in a pressure bottle and the mixture was agitated at 50°C for 8 hours. After the reaction, 10 ml ethanol was added to the reaction mixture. Fractional distillation of the reaction product(5.5 g) gave N,N-diethyl-(but-2-enyl)amine(3.4 g) at bp 43-45°C/20 mmHg and N,N-diethyl(octa-cis-2,6-dienyl)amine(2.0 g) at bp 50-52°C/1.5 mmHg. Separation and identification of stereoisomers were achieved by i.r., n.m.r. and mass spectra after g.l.c. fractionation. N,N-Diethyl(but-2-enyl)amine contained cis (1) and trans (2) (in the ratio 24:1), and N,N-diethyl(octa-cis-2,6-dienyl)amine contained N,N-diethyl(octa-cis-2,cis-6-dienyl)amine (3) and N,N-diethyl(octa-cis-2,trans-6-dienyl)amine (4) (in the ratio 7:3). The structure of (3) and (4) were supported by the following data<sup>7</sup>).

(3): mass spectra; m/e 181 (M<sup>+</sup>), i.r. spectra (cm<sup>-1</sup>; neat); 715, 695 (-CH=C-), n.m.r. spectra (τ; CCl<sub>4</sub>); 9.03(6H, t, J=7.2 Hz, CH<sub>3</sub>-CH<sub>2</sub>-), 8.42(3H, d, J=4.8 Hz, CH<sub>3</sub>-C=), 7.92-8.10(4H, m, =C-CH<sub>2</sub>-CH<sub>2</sub>-C=), 7.58(4H, q, J=7.2 Hz, >N-CH<sub>2</sub>-CH<sub>2</sub>),

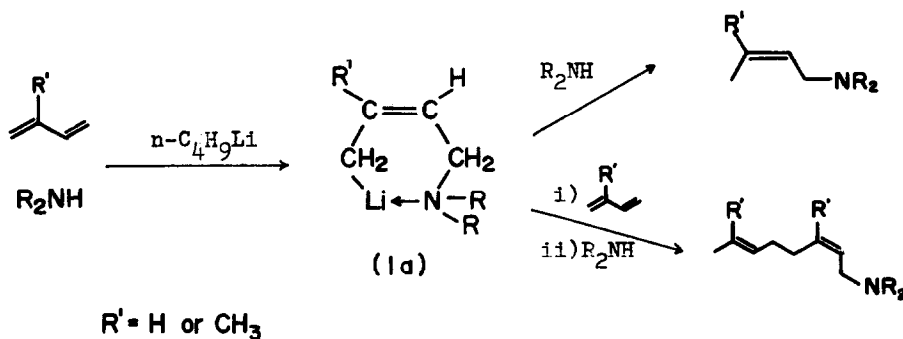
7.03(2H, d,  $J=4.5$  Hz,  $>N-CH_2-C=$ ), 4.25-5.00(4H, m,  $-CH=CH-$ ).

(4): mass spectra;  $m/e$  181 ( $M^+$ ), i.r. spectra( $cm^{-1}$ ;neat); 963 ( $-CH^{\ddagger}CH-$ ), 690 ( $-CH^{\underline{c}}CH-$ ), n.m.r. spectra( $\tau$ ;  $CCl_4$ ); 9.03(6H, t,  $J=7.2$  Hz), 8.40(3H, d,  $J=4.8$  Hz), 7.92-8.15(4H, m), 7.58(4H, q,  $J=7.2$  Hz), 7.02(2H, d,  $J=4.5$  Hz,  $>N-CH_2-C=$ ), 4.30-4.80(4H, m).

Similarly the reaction of isoprene with diethylamine was found to result in the stereoselective formation of *N,N*-diethyl(3,7-dimethylocta-*cis*-2,6-dienyl)amine (*N,N*-diethyl nerylamine) (8)<sup>8)</sup> owing to head to tail dimerization of isoprene. (Table 2).

(8): mass spectra;  $m/e$  209 ( $M^+$ ), i.r. spectra( $cm^{-1}$ ;neat); 830 ( $-\overset{\cdot}{C}=CH-$ ), n.m.r. spectra( $\tau$ ;  $CCl_4$ ); 9.04(6H, t,  $J=7.0$  Hz,  $CH_3-CH_2-$ ), 8.24-8.47(6H, m,  $CH_3-C=$ ), 7.89-8.09(4H, m,  $=C-CH_2-CH_2-C=$ ), 7.62(4H, q,  $J=7.0$  Hz,  $>N-CH_2-CH_3$ ), 7.09(2H, d,  $J=6.0$  Hz,  $>N-CH_2-C=$ ), 4.65-5.18(2H, m,  $-\overset{\cdot}{C}=CH-$ ).

Stereoselective formations of these octa-*cis*-2,6-dienylamine derivatives may be explained by considering a lithio-intermediate having a coordinate lithium-nitrogen bond as shown in (1a)<sup>9)</sup>.



On the contrary, in the case of sodium-catalyzed reaction, the selectivity of *N,N*-dialkyl(octa-*cis*-2,6-dienyl)amine derivatives in the  $n=2$  telomers was low, and the other 1,4-coupled and 1,3-coupled telomers were also given. (Table 1 and 2).

This reaction may be applied to other *sec*-amines such as dimethylamine, di-*n*-propylamine, piperidine and morpholine.

TABLE 1. Telomerizations of Butadiene with sec-Amines<sup>a)</sup>

sec-Amine	Cat.	Temp. (°C)	Time (hr.)	Product (g)	Composition of Telomers (%)					
					(1)	(2)	(3)	(4)	(5) <sup>b)</sup>	n <sub>2</sub> 3
Et <sub>2</sub> NH	n-C <sub>4</sub> H <sub>9</sub> Li	50	8	5.5	59	2	27	11	-	1
Et <sub>2</sub> NH	n-C <sub>4</sub> H <sub>9</sub> Li	40	4	3.1	85	2	9	4	-	t
Et <sub>2</sub> NH	Na <sup>c)</sup>	40	2	5.7	15	48	10 <sup>d)</sup>		15	12
Me <sub>2</sub> NH	n-C <sub>4</sub> H <sub>9</sub> Li	45	5	4.2	28	27	25	9	1	9

a) Reaction condition; sec-amine (0.05 mol), 1,3-diene (0.15 mol), benzene (20 ml), ether (6.5 ml) solution of n-C<sub>4</sub>H<sub>9</sub>Li (0.01 mol).

b) This compound was identified to be N,N-dialkyl(2-vinylhexa-4-enyl)amine by i.r., n.m.r. and mass spectra.

c) This catalyst(0.1 g) was added with ether (6.5 ml).

d) This was found to be a mixture of N,N-diethyl(octa-cis and trans-2,6-dienyl) amines by n.m.r. spectra.

TABLE 2. Telomerizations of Isoprene with sec-Amines<sup>a)</sup>

sec-Amine	Cat.	Temp. (°C)	Time (hr.)	Product (g)	Composition of Telomers (%) <sup>b)</sup>				
					(6)	(7)	(8)	(9)	n <sub>2</sub> 3
Et <sub>2</sub> NH	n-C <sub>4</sub> H <sub>9</sub> Li	65	8.5	6.5	77	6	17	-	1
Et <sub>2</sub> NH	n-C <sub>4</sub> H <sub>9</sub> Li	55	9	6.3	87	5	7	-	1
Et <sub>2</sub> NH	Na <sup>c)</sup>	55	4	6.9 <sup>d)</sup>	53	28	8	2	3
Me <sub>2</sub> NH	n-C <sub>4</sub> H <sub>9</sub> Li	60	5.5	3.9 <sup>e)</sup>	53	11	31	1	1

a) Ref. Table 1. a).

b) (6): N,N-dialkyl(3-methylbut-2-enyl)amine, (7): N,N-dialkyl(2-methylbut-2-enyl)amine, (9): N,N-dialkyl(2-isopropenyl-5-methylhex-4-enyl)amine.

c) Ref. Table 1. c).

d) This product contained 2% of N,N-diethyl geranylamine and 4% of other Et<sub>2</sub>N(C<sub>10</sub>H<sub>16</sub>).

e) This product contained 3% of C<sub>10</sub>H<sub>16</sub>.

## References and Footnotes

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- 6) It has been reported that the n-butyl lithium-catalyzed addition reaction of diethylamine to butadiene gave N,N-diethyl(but-cis-2-enyl)amine and a small amount of N,N-diethyl(but-trans-2-enyl)amine. (N. Imai, T. Narita, and T. Tsuruta, Tetrahedron Lett., 3517 (1971).)
- 7) The double bond ( $-C=C-C-NR_2$ ) in (3) and (4) have been assigned cis on the basis of the following data of N,N-diethyl(but-2-enyl)amine. (1): n.m.r. ( $\tau$ ); 7.03(2H, d,  $J=4.5$  Hz,  $-\overset{1}{\text{C}}\text{H}=\overset{2}{\text{C}}\text{H}-\text{CH}_2-\text{NR}_2$ ), i.r. ( $\text{cm}^{-1}$ ); 690 ( $-\overset{1}{\text{C}}\text{H}=\overset{2}{\text{C}}\text{H}-$ ). (2): n.m.r. ( $\tau$ ); 7.11(2H, d,  $J=4.0$  Hz,  $-\overset{3}{\text{C}}\text{H}=\overset{4}{\text{C}}\text{H}-\text{CH}_2-\text{NR}_2$ ), i.r. ( $\text{cm}^{-1}$ ); 965 ( $-\overset{3}{\text{C}}\text{H}=\overset{4}{\text{C}}\text{H}-$ ).
- 8) The data of i.r., n.m.r. and mass spectra agreed completely with the authentic N,N-dialkyl nerylamine.
- 9) Such a coordinate lithium-nitrogen bond has been also reported in the reaction of the direct lithiation of N,N-dimethyl-3-ethenylamine or N,N-dimethylbenzylamine. (F. N. Jones, M. F. Zenn, and C. R. Hauser, J. Org. Chem., 28, 663, 3461 (1963); D. Slocum, and P. L. Gierer, Chem. Commun., 305 (1971).)