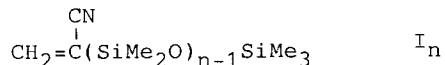


### Convenient Synthetic Routes to $\alpha$ -Oligosiloxanylacrylonitriles

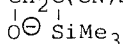
Yuhsuke Kawakami\*, Hirofumi Hisada, and Yuya Yamashita  
Department of Synthetic Chemistry  
Faculty of Engineering, Nagoya University  
Chikusa, Nagoya 464, Japan

**Abstract:** Novel 1,4-elimination reaction of C,N-bis(trimethylsilyl)-C-trimethylsiloxymethylketenimine and retro Diels-Alder reaction of 2-oligosiloxanyl-5-norbornene-2-carbonitrile cleanly gave  $\alpha$ -oligosiloxanylacrylonitriles in excellent yield.

During our studies on vinyl-polymerizable oligosiloxanes, we became interested in  $\alpha$ -oligosiloxanylacrylonitriles ( $I_n$ ).



Such new compounds, representatively  $\alpha$ -trimethylsilylacrylonitrile ( $I_1$ ), might be prepared by several methods. However, several attempts to synthesize  $I_1$ , including the reaction of tris(trimethylsilyl)ketenimine with formaldehyde, were unsuccessful. If we consider the intermediate of expected Peterson reaction as  $\text{CH}_2\overset{\ominus}{\text{C}}(\text{CN})\text{SiMe}_3$ , 3-trimethylsiloxypropionitrile might be used as a



starting material for the synthesis of  $I_1$ . When 3-hydroxypropionitrile was treated with three equivalents of LDA followed by slight excess trimethylchlorosilane, C-trimethylsiloxymethyl-C,N-bis(trimethylsilyl)ketenimine (II) was obtained in 75% yield. bp 47.7-48.8 °C/0.15 mmHg. Treatment of II with a Lewis acid in dichloromethane at -78 °C cleanly gave the desired compound  $I_1$  in excellent yield.

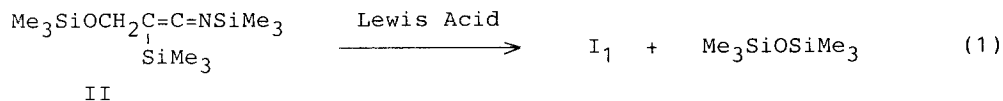
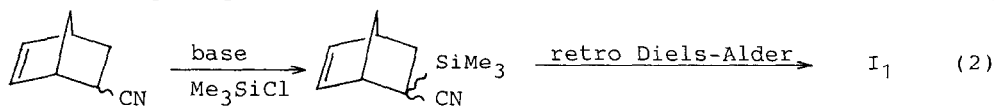


Table 1. Catalytic Activity of Various Lewis Acids in the 1,4-Elimination Reaction of II.

No. Lewis Acid	Yield(%)		No. Lewis Acid	Yield(%)	
	GC	Isol'd		GC	Isol'd
1. BF <sub>3</sub> Et <sub>2</sub> O	quant.	88	6. ZnCl <sub>2</sub>	87	47
2. AlCl <sub>3</sub>	85	40	7. MgCl <sub>2</sub>	39	-
3. AlBr <sub>3</sub>	32	-	8. CdCl <sub>2</sub>	47	-
4. FeCl <sub>3</sub>	quant.	-	9. CuCl <sub>2</sub>	29	-
5. SnCl <sub>4</sub>	41	-	10. CuBr	95	-

In order to improve the disadvantage of the reaction (1) that two silicon containing groups were abandoned in the reaction, retro Diels-Alder reaction of 2-trimethylsilyl-5-norbornene-2-carbonitrile was studied (reaction 2).



The reaction proceeded very nicely at 190°C. Simple purification of the pyrolyzate by short column chromatography gave the products in excellent yields.<sup>3)</sup> These reactions will find wide applications in the syntheses of  $\alpha$ -alkyl substituted acrylonitriles.

Table 2. Retro Diels-Alder Reaction Leading to  $\alpha$ -Substituted Acrylonitriles.

No. Substituent at $\alpha$ -carbon	Yield (%)	Thermolysis Temp.(°C)	No. Substituent at $\alpha$ -carbon	Yield (%)	Thermolysis Temp.(°C)
1. Me <sub>3</sub> Si	75	190	6. Me <sub>3</sub> SiOSiMe <sub>2</sub> CH <sub>2</sub>	57	190
2. Me <sub>3</sub> SiOSiMe <sub>2</sub>	81	190	7. CH <sub>3</sub> CH <sub>2</sub>	60	220
3. Me <sub>3</sub> Si(OSiMe <sub>2</sub> ) <sub>2</sub>	85	190	8. C <sub>6</sub> H <sub>5</sub>	n.r.	-
4. Me <sub>3</sub> Si(OSiMe <sub>2</sub> ) <sub>3</sub>	81	190	9. C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	67	220
5. Me <sub>3</sub> SiCH <sub>2</sub>	76	190			

This work was partially supported by Grant in Aid for Scientific Research (60550639) from Ministry of Education, Science and Culture.

## References

- H. Okada, I. Matsuda, and Y. Izumi, Chem. Lett., 97(1983).
- I. Matsuda, H. Okada, and Y. Izumi, Bull. Chem. Soc. Jpn., 56, 528(1983).
- <sup>1</sup>H NMR in  $\delta$ (CDCl<sub>3</sub>) values : I<sub>1</sub> 0.21(CH<sub>3</sub>), 6.03, 6.40(two d, J=2.4 Hz, vinylidene). I<sub>2</sub> 0.09(Si(CH<sub>3</sub>)<sub>3</sub>), 0.26(=Si(CH<sub>3</sub>)<sub>2</sub>), 6.09, 6.42(two d, J=2.4 Hz, vinylidene). I<sub>3</sub>, I<sub>4</sub> 0.05(Si(CH<sub>3</sub>)<sub>3</sub>), 0.09(OSi(CH<sub>3</sub>)<sub>2</sub>), 0.32(=Si(CH<sub>3</sub>)<sub>2</sub>), 6.17, 6.47(two d, J=2.4 Hz, vinylidene). The products from runs # 5 and 6 in Table 2 show <sup>1</sup>H NMR signals at 0.01(Si(CH<sub>3</sub>)<sub>3</sub>), 1.64(methylene), 5.34(with long range coupling) and 5.51(vinylidene), and 0.12(Si(CH<sub>3</sub>)<sub>3</sub>), 0.22(CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>), 1.78(methylene), 5.42(with long range coupling) and 5.62(vinylidene), respectively.

(Received in Japan 14 September 1985)