

Cationic Telomerization of Olefin with Isocyanide

Among these products, **7** and **8** are the isomer and isomerized dimer, both of which are produced from *t*-butyl isocyanide with BF_3OEt_2 in the absence of vinyl ether. The products of **9a**, **10a** and **11a** are the 1 : 1, 1 : 2 and 1 : 3 telomers, respectively, which consist of the vinyl ether taxogen and the *t*-butyl isocyanide telogen. It is of interest to note that the direction of bonding of the CN group in the telomers is opposite to that of the isocyanide telogen. The telomers having the same back-bone structure were formed also in the free-radical telomerization of olefins with *t*-butyl isocyanide.³ The IR spectra of these telomers are shown in Figure 1. The product **12a** may be regarded as a 2 : 1 telomer; *i.e.*, it consists of one mole of vinyl ether and two moles of *t*-butyl isocyanide.

With reference to the mechanistic scheme of the cationic isomerization and oligomerization of tertiary alkyl isocyanide,² the formations of

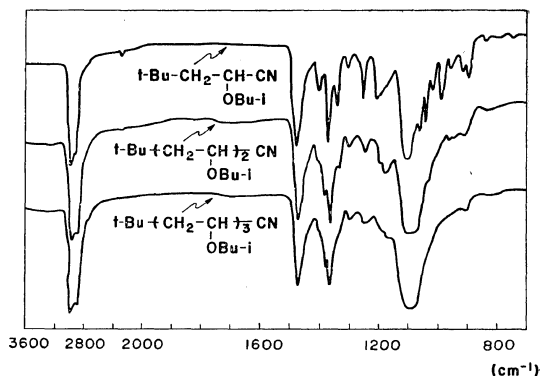


Figure 1. The IR spectra of telomers.

the six products of the present reaction are schematized in Diagram I. The elementary reactions in this diagram are the additions of a cation to one of two nucleophiles, isocyanide and vinyl ether, and the β -scissions of imidoyl

Diagram I

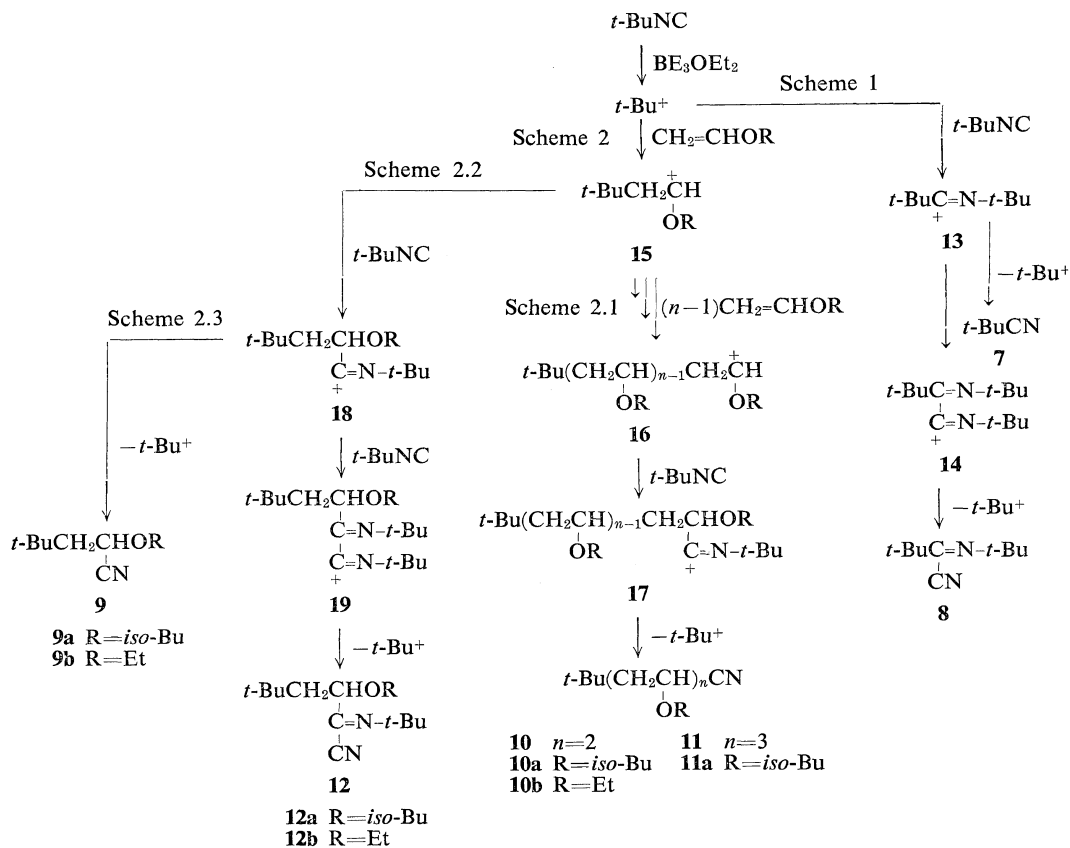
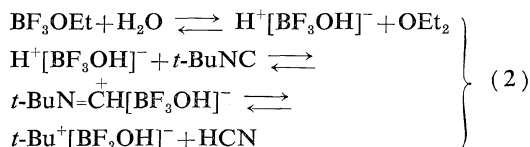
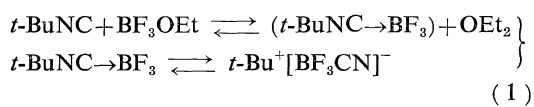


Table I. Cationic telomerization of isobutyl vinyl ether with *t*-butyl isocyanide as telogen using BF_3OEt_2 catalyst^a

Products	Yield, %
<i>t</i> -BuCN (7)	47
<i>t</i> -Bu-C=N- <i>t</i> -Bu CN	31
<i>t</i> -Bu-CH ₂ CHCN O <i>iso</i> -Bu (9a)	3
<i>t</i> -Bu-(CH ₂ CH) ₂ -CN O <i>iso</i> -Bu (10a)	4.5
<i>t</i> -Bu-(CH ₂ CH) ₃ -CN O <i>iso</i> -Bu (11a)	4.5
<i>t</i> -Bu-CH ₂ CH-C=N- <i>t</i> -Bu (12a) O <i>iso</i> -Bu	5

^a Telomerization conditions: *t*-BuNC, 112 mmol; $\text{CH}_2=\text{CHO}$ *iso*-Bu, 76 mmol, BF_3OEt_2 , 7 mmol; CH_2Cl_2 , 50 ml; One day's duration, at room temp.

cations regenerating the *t*-butyl cation. Every scheme is a combination of these elementary reactions, which start with the addition of a *t*-butyl cation to a nucleophile and end with the regeneration of a *t*-butyl cation. As to the initial generation of the *t*-butyl cation complex, two possible processes may be assumed, *i.e.*, the direct interaction of *t*-butyl isocyanide with BF_3OEt_2 (eq 1) and the participation of a protonic acid due to a small amount of water impurity (eq 2).

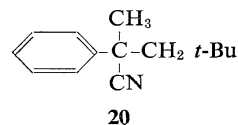


In scheme 1, the addition of a *t*-butyl cation to *t*-butyl isocyanide produces an imidoyl cation **14** whose decomposition gives **7**. The addition of **13** to the second molecule of *t*-butyl isocyanide yields another imidoyl cation **14** which decomposes into **8** and *t*-butyl cation. Scheme 2 is the course of telomerization, which is initiated by the attack of the *t*-butyl cation on vinyl ether

affording a cation **15**. Successive additions of **15** to one and two molecules of vinyl ether followed by the addition of **16** ($n=2$ and 3) to *t*-butyl isocyanide give rise to two telomers of **10** and **11**. The formation of **9** is explained by the sequence of **15** to **18** to **9**. The sequence of **15** to **18** to **19** ends with the production of **12**.

Scheme 1 and 2 bifurcate according to the additions of *t*-butyl cation to isocyanide and vinyl ether, respectively. The combined yield of **7** and **8** is higher than that of the products from **9** to **12**. This fact suggests that *t*-butyl isocyanide is more nucleophilic than vinyl ether.

Styrene is also a cationically polymerizable monomer, which, however, does not enter into the reaction with isocyanide. Only **7** and **8** were produced in the treatment of a mixture of *t*-butyl isocyanide and styrene with a catalyst of BF_3OEt_2 . Also in the case of *p*-methoxystyrene, no telomer was formed. However, α -methylstyrene was reacted with *t*-butyl isocyanide to produce an 1:1 adduct of **20**. The formation of **20** is rationalized by scheme 2.2 and 2.3 in Diagram I.



EXPERIMENTAL

Reagents

t-Butyl isocyanide was prepared according to Ugi's procedure.⁴ Commercial methylene chloride, isobutyl vinyl ether, ethyl vinyl ether, 4,5-dihydropyran and α -methyl styrene were purified by the usual methods. Commercial borontrifluoride etherate (BF_3OEt_2) was used without purification.

Telomerization of Isobutyl Vinyl Ether with *t*-Butyl Isocyanide as Telogen

Under nitrogen atmosphere at room temperature, 7 mmol of BF_3OEt_2 in 7 ml of methylene chloride was added dropwise to a mixture of 10 ml (112 mmol) of *t*-butyl isocyanide and 10 ml (76 mmol) of isobutyl vinyl ether in 50 ml of methylene chloride. An exothermic reaction

began immediately, and the reaction mixture turned red-brown. The mixture was allowed to stand at room temperature for one day, and then was quenched with aqueous sodium bicarbonate. The methylene chloride layer was subjected to distillation. From the fractions of distillation, four products, **9a**, **10a**, **11a** and **12a**, were isolated by preparative GLPC. The amounts of **7** and **8** were determined by GLPC analysis using the corresponding authentic samples.

From the first fraction (bp 87°C (10 mm)), 2-isobutoxy-4,4-dimethylvaleronitrile (**9a**) was obtained by means of preparative GLPC in a yield of 3%. NMR (CDCl₃): τ 5.90 (1H, triplet, $-\text{CH}(\text{CN})-\text{O}-$), 6.65 (2H, multiplet, $-\text{OCH}_2-\text{CH}$), 7.8—8.5 (3H, complex multiplet, $-\text{OCH}_2-\text{CH}(\text{CH}_3)_2$, $t\text{-Bu}-\text{CH}_2-$), 9.00 (9H, singlet, $t\text{-Bu}-$), and 9.05 ppm (6H, doublet, $-\text{CH}_2\text{CH}(\text{CH}_3)_2$).

Anal. Calcd for C₁₁H₂₁NO: C, 72.08, H, 11.55; N, 7.64. Found: C, 72.14; H, 11.36; N, 7.55.

From the second fraction (bp 100—120°C (3.5 mm)), the 1:2 telomers (**10a**) and (**12a**) were obtained by means of preparative GLPC, in yields of 4.5% and 5%, respectively. 2,4-Diisobutoxy-6,6-dimethylheptanenitrile (**10a**). NMR (CDCl₃): τ 5.75 (1H, triplet, $-\text{CH}(\text{CN})-\text{O}-$), 6.2—7.1 (5H, complex multiplet, $-\text{CH}_2\text{CH}-\text{O}-\text{CH}_2-$ and $-\text{CH}(\text{CN})-\text{O}-\text{CH}_2-$), 7.8—8.8 (6H, complex multiplet, $t\text{-Bu}-\text{CH}_2-$, $2 \times -\text{OCH}_2-\text{CH}(\text{CH}_3)_2$ and $\text{CH}-\text{CH}_2-\text{CH}(\text{CN})-\text{O}-$, and 8.9—9.2 ppm (21H, complex multiplet, $t\text{-Bu}-\text{CH}_2-$, and $2 \times -\text{OCH}_2-\text{CH}(\text{CH}_3)_2$).

Anal. Calcd for C₁₇H₃₃NO₂: C, 72.04; H, 11.74; N, 4.94. Found: C, 72.17; H, 11.97; N, 4.81. 2-*t*-Butylimino-3-isobutoxy-5,5-dimethylcapronitrile (**12a**). IR (neat): 2200 ($\nu_{\text{C}=\text{N}}$) and 1625 cm⁻¹ ($\nu_{\text{C}=\text{N}}$). NMR (CDCl₃): τ 6.08 (1H, multiplet, $-\text{CH}(\text{CN})\text{O}$), 6.85 (2H, doublet, $-\text{O}-\text{CH}_2-$), 8.0—8.8 (3H, complex multiplet, $-\text{OCH}_2-\text{CH}(\text{CH}_3)_2$ and $t\text{-Bu}-\text{CH}_2-$), 8.58 (9H, singlet, $t\text{-Bu}-\text{N}=\text{C}-$), 9.03 (9H, singlet, $t\text{-Bu}-\text{CH}_2-$), and 9.10 ppm (6H, doublet, $(\text{CH}_3)_2\text{CH}-$).

Anal. Calcd for C₁₆H₃₀N₂O: C, 72.13; H, 11.35; N, 10.52. Found: C, 71.55; H, 11.60; N, 9.94.

From the third fraction (bp 140—164°C (3.5

mm)), the 1:3 telomer, 2,4,6-triisobutoxy-8,8-dimethylnonanenitrile (**11a**), was isolated by means of preparative GLPC in a yield of 4.5%. NMR (CDCl₃): similar to 1:2 adduct (**10a**).

Anal. Calcd for C₂₃H₄₅NO₃: C, 72.01; H, 11.82; N, 3.65. Found: C, 72.24; H, 12.03, N, 3.46.

*Telomerization of Ethyl Vinyl Ether with *t*-Butyl Isocyanide as Telogen*

The reaction procedure was almost the same as that described above. The distillate was analyzed by GLPC and the four telomerization products were isolated by preparative GLPC. 2-Ethoxy-4,4-dimethylvaleronitrile (**9b**, 1:1 telomer) was obtained from the distillate boiling 90—92°C (24 mm) in a yield of 4%. IR (neat): 2230 cm⁻¹ ($\nu_{\text{C}=\text{N}}$). NMR (CDCl₃): τ 5.83 (1H, triplet, $-\text{CH}(\text{CN})\text{O}-$), 6.32 (2H, multiplet, $-\text{OCH}_2-$), 8.17 (2H, doublet, $t\text{-Bu}-\text{CH}_2-$), 8.73 (3H, triplet, $\text{CH}_3\text{CH}_2\text{O}$), and 8.98 ppm (9H, singlet, $t\text{-Bu}-$).

Anal. Calcd for C₉H₁₇NO: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.76; H, 11.23; N, 8.86. 2-*t*-Butylimino-3-ethoxy-5,5-dimethylcapronitrile (**12b**, 2:1 telomer) was obtained from the distillate boiling at 70—80°C (4 mm) in a yield of 3%. IR (neat): 2200 ($\nu_{\text{C}=\text{N}}$) and 1625 cm⁻¹ ($\nu_{\text{C}=\text{N}}$). NMR (CDCl₃): τ 5.98 (1H, multiplet, $-\text{CHOCH}_2$), 6.50 (2H, multiplet, $-\text{OCH}_2\text{CH}_3$), 8.35 (2H, multiplet, $t\text{-BuCH}_2-$), 8.55 (9H, singlet, $t\text{-BuN}=\text{C}-$), 8.75 (3H, triplet, $\text{CH}_3\text{CH}_2\text{O}-$), and 8.98 ppm (9H, singlet, $t\text{-BuCH}_2-$).

Anal. Calcd for C₁₄H₂₆N₂O: C, 70.54; H, 10.99; N, 11.75. Found: C, 70.27; H, 11.25; N, 11.67. 2,4-Diethoxy-6,6-dimethylheptanenitrile (**10b**, 1:2 telomer) was obtained from the distillate boiling at 95—100°C (4 mm) in a yield of 4%. NMR (CDCl₃): τ 5.70 (1H, triplet, $-\text{CH}(\text{CN})-\text{O}-$), 6.0—6.8 (5H, complex multiplet, $-\text{CH}_2\text{CH}-\text{OCH}_2-$ and $-\text{CH}(\text{CN})-\text{O}-\text{CH}_2-$), 7.8—8.4 (4H, complex multiplet, $t\text{-BuCH}_2-$ and $-\text{CH}-\text{CH}_2-\text{CH}$), and 8.4—9.0 ppm (6H, complex multiplet, $2\text{CH}_3\text{CH}_2\text{O}-$), 9.03 (9H, singlet, $t\text{-Bu}$).

Anal. Calcd for C₁₃H₂₅NO₂: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.43; H, 11.27; N, 5.92.

*Reaction of 4,5-Dihydropyran with *t*-Butyl Isocyanide*

cis-2-Cyano-3-*t*-butyl-tetrahydropyran was obtained from the reaction of 4,5-dihydropyran with *t*-butyl isocyanide in a yield of 4% (bp 90–92°C (8 mm)). NMR (CDCl₃): τ 5.18 (1H, multiplet, $J=3.0$ Hz, -OCH-CN), 6.15 (2H, multiplet, -CH₂-O-), 8.0–8.8 (5H, multiplet, *t*-Bu-CH-CH₂-CH₂-), and 8.97 ppm (9H, singlet, *t*-Bu).

Anal. Calcd for C₁₀H₁₇NO: C, 71.81; H, 10.25; N, 8.38. Found: C, 70.96; H, 10.18; N, 8.37.

*Reaction of α -Methylstyrene with *t*-Butyl Isocyanide*

2-Phenyl-2,4,4-trimethylvaleronitrile (**20**) was obtained at a yield of 2% in the reaction of *t*-butyl isocyanide with α -methylstyrene according to the above procedure. IR (neat): 2230 cm⁻¹

($\nu_{C\equiv N}$) NMR (CDCl₃): τ 2.40–2.90 (5H, multiplet, phenyl), 8.00 (2H, singlet, -CH₂-), 8.25 (3H, singlet, CH₃), and 9.14 ppm (9H, singlet, *t*-Bu).

Anal. Calcd for C₁₄H₁₉N: C, 83.53; H, 9.51; N, 6.96. Found: C, 81.89; H, 9.47; N, 7.31.

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