DAEHAN HWAHAK HWOEJEE (Journal of the Korean Chemical Society) Vol. 24, No. 3, 1980 Printed in the Republic of Korea

이소니트릴의 자유라디칼반용

金 性 洙*

미국 남가주대학교 화학과 (1980. 4. 10 접수)

Homolytic Reactions of Isonitriles

Sung Soo Kim*

Department of Chemistry, University of Southern California, Los Angeles, California 90007, U.S.A.

(Received April 10, 1980)

요 약. 여러종류의 자유라디칼들이 이소니트릴에 첨가되어 중간체인 imidoyl 자유라디칼 RN= ČR'을 형성한다. 이것은 또한 imine 으로부터 imidoyl hydrogen을 떼어 내는 다음과 같은 반응에 의해서도 생성될 수 있다.

$$H$$

$$RN = CR' + R'' \cdot \longrightarrow RN = CR' + R'' - H$$

중간체인 imidoyl 자유라디칼은 β-cleavage 및 atom transfer 반응을 통해서 안정된 분자를 형성한다. β-Cleavage는 imidoyl 자유라디칼의 구조에 따라서 두개의 다른 방향으로의 반응이 가능하다. Cyanide transfer와 소위 말하는 정상적인 β-cleavage가 그러한 반응들이다.

t-Butoxy 자유라디칼이 t-butylisonitrile 7에 첨가되면 중간체인 t-Bu-N=Ċ-O-Bu-t가 생성되는데, 이것은 β-cleavage 반응을 통해서 t-butylisocyanate 와 t-butyl 자유라디칼을 형성한다.

Phenyl 자유라디칼은 7에 첨가되어 중간체인 t-Bu-N= $\dot{\mathbf{C}}$ - C_6H_5 를 형성하는데 이것은 cyanide transfer 반응을 통해서 benzonitrile 과 t-butyl 자유라디칼로 분해된다. 여기서 생성되는 t-butyl 자유라디칼은 다시 7에 첨가하여 intermediate 인 자유라디칼 t-Bu-N= $\dot{\mathbf{C}}$ -Bu-t을 형성하고, 이것은 다시 pivalonlonitrile 과 t-butyl 자유라디칼로 분해되는데 이러한 반응이 반복되므로 radical chain isomerization 을 일으킨다.

Silyl 자유라디칼은 7에 첨가되어 t-Bu-N=Ć-Si(CH₃)3 를 형성하고, 이것은 cyanide transfer 반응을 거쳐서 다시 (CH₃)3SiCN 과 t-butyl 자유라디칼로 분해된다.

ABSTRACT. Various radicals may add to isonitriles to give imidoyl radcals RN=CR'. This may be also generated via abstraction of imidoyl hydrogen from imine in the following manner:

$$RN = \stackrel{!}{C}R' + R'' \cdot \longrightarrow RN = \stackrel{!}{C}R' + R'' - H$$

Imidoyl radicals would be stabilized via two pathways, β -cleavage and atom transfer reactions. β -Cleavage may occur in two directions depending upon structure of the radicals. Cyanide transfer and the "so-called" normal β -cleavage are the two modes of β -cleavage.

Addition of t-butoxy radical to t-butyl isocyanide 7 generates an imidoyl radical t-Bu-N= \dot{C} -O-Bu-t, which undergoes β -cleavage to give t-butyl isocyanate and t-butyl radical. Addi-

^{*}Present Address: Korea Reseurch Institute of Chemical Technology(한국화학연구소), Daeduck 300-32, Korea

tion of phenyl radical to 7 forms the intermediate radical t-Bu-N= \dot{C} -C₆H₅, which decomposes to give benzonitrile and t-butyl radical. The t-butyl radical generated from the β -cleavage adds to 7 giving the radical t-Bu-N= \dot{C} -Bu-t, which cleaves only to pivalonitrile and t-butyl radical, inducing radical chain isomerization. Trimethylsilyl radical adds to 7 to give the intermediate t-BuN= \dot{C} -Si(CH₃)₃, which collapses to (CH₃)₃ SiCN and a t-butyl radical.

INTRODUCTION

Isonitriles¹ are the only class of stable organic compounds containing formally divalent carbon, the structure of which is considered to be a hybrid of resonance structures 1a and 1b.

$$R - \overset{\cdot \cdot}{\underset{1a}{}} = C : \longleftrightarrow R - \overset{\cdot \cdot}{\underset{1b}{}} C :$$

While wide range of reactions of isonitriles have been known and synthetically utilized, free radical reactions have received only limited attention^{2~4}. As the driving force of addition reaction to olefinic bonds originates from the tendency of carbon atom to expand its sp²- to sp³-hybridization, the terminal divalent carbon atom tends to achieve tetra-valency via reactions. It is this factor that various radical species may add to the isonitriles thereby con-

stituting the homolytic reactions. The key intermediate is imidoyl radical of which the carbon radical centre has the identical electronic configuration with vinyl and acyl radicals. ESR study^{5,6} indicates that imidoyl radicals are sigma type.

The radicals would be generated in two different ways and may be stabilized via three reaction pathways based on the studies so far reported, which is shown in Scheme 1.

In the present study, we have generated various imidoyl radicals and wish to discuss the reactions in terms of energetics on the basis of formation of products.

RESULTS AND DISCUSSION

Imidoyl Radical 2a from Imine 3a. N-Neopentylidene t-butylamine 3a was prepared

$$R^{1}N \equiv C \xrightarrow{(1a)} R^{1}-N = \hat{C}-XY \leftarrow \frac{R^{2}}{(1b)} R^{1}N = \hat{C}-XY$$

$$1 \qquad 2 \qquad 3$$

$$R^{1}-N = \hat{C}-XY \qquad \qquad Cyanide Transfer \longrightarrow R^{1} + NC-XY$$

$$\beta - Cleavage \longrightarrow R^{1}N = C = X + Y \qquad (3)$$

$$H \longrightarrow R^{1}N = C - XY \qquad (4)$$

$$Scheme 1.$$

Table 1. Formation of pivalenitrile during thermolysis of 3a in the presence of decomposing TBP at 125 °C. "

Reaction time (min.)	20	40	70	120	170
mmoles of t-BuO· generated ^b mmoles of t-Bu-CN formed	7.49	14. 69	25. 0	41. 0	55. 45
	0.92	2. 19	3. 18	4. 70	6. 40

^a Formation of pivalonitirile was monitored by VPC using 11ft, 20% TCEP on Chromosorb P column at 60°C, inj. port 100°C. Toluene was added to the samples before injection as an internal standard. TBP did not decompose significantly during the VPC analysis.

⁵ Decomposition of TBP was calculated according to the equation, $k=10^{13}e^{-E_a/RT}\sec^{-1}$ where $E_a=37$ kcal/mole.

$$t-Bu-N=CH-Bu-t \xrightarrow{t-BuO} t-Bu-N=C-Bu-t + t-BuOH$$

$$3a \qquad 2a \qquad t-BuCN + t-Bu$$

$$t-Bu-N=C+Bu-t \xrightarrow{t-BuCN} t-BuNC + t-Bu$$

$$7 \qquad (6)$$

$$Scheme 2.$$

by reaction of pivalaldehyde with t-butyl a-mine^{7,8}. Reaction at $125\,^{\circ}\text{C}$ of degassed and sealed Pyrex ampoules containing 3a with $0.1\,M$ t-butylperoxide (TBP) in chlorobenzene led to the formation of pivalonitrile in Table 1. Pivalonitrile would be formed via Scheme 2.

The abstraction of imidoyl hydrogen from 3a by t-butoxy radical generates 2a, which has two ways of stabilization, one leading to the formation of 6 and the other 7. The absence of 7 even at very short interval corresponding to $\langle 1\% \rangle$ TBP decomposition exclude the latter pathway. The partion of 2a to 6 is consistent with the relative stabilities of isomeric isonitrile and nitrile structures since the heats of formation of the latter are more favorable by $15\sim 25 \text{ kcal/mole}^9$.

It is clear from Table 1, that 6 is not formed via chain mechanism. t-Butyl radical expelled from 2a would not be reactive enough to abstract imidoyl hydrogen from 3a as the chain carrier. This might be also interpreted as being due to the comparable bond strengths of $(CH_3)_3C$ -H and imidoyl carbon-hydrogen bond in $(CH_3)_3CN = C$ $(CH_3)_3$.

Addition of t-Butoxy and Pheyl Radicals to t-Butylisocyanide 7. We have shown that t-butoxy¹⁰ and phenyl¹¹ radicals add to 7 to give imidoyl radicals 2b and 2c, respectively. We further compared the facility of the addition reactions with other well-defined free radical reactions in the following manner.

Reaction of degassed and sealed Pyrex tubes

containing variable molar concentration of 7 and cumene (as competitive scavengers of t-butoxy or phenyl radical) with t-butyl peroxide (TBP) or benzoyl peroxide (BP) in chlorobenzene led to formation of the products. These were quantitatively analyzed by VPC technique as shown in Table 2.

We10 have shown that 7 and cumene have comparable capacity as the free radical scavengers towards t-butoxy radical thereby k_{8a}/k_9 = 0.84 at 398 °K. The intermediate 2 b, we indicated, collapsed to 8 and t-butyl radical via direction A. However same products might have been obtained via direction B14 in the following manner. If 2b fragmented via B, t-Bu-O-C≡N and t-butyl radical might have been formed. Unstable t-Bu-O-C \equiv N, in turn, may rapidly rearrange itself to give 8. This route, however, has been ruled out by Roberts et al. 6 When t-C₄D₉OO-C₄D₉-t was employed as a source of perduterio-t-butoxy radicals only perdeuterio-t-butyl radicals and no t-butyl radicals were detected.

Addition of phenyl radical to 7 takes place much faster than hydrogen transfer to the radical from cumene, thus $(k_{10a}/k_{1I}) = 7.1$ at 373° K. ¹¹

A control experiment showed 7 does not isomerize to 6 for extended periods at 398 °K or 373°K in the absence of the initiators. Thus eq. (12) makes a very efficient radical chain reaction since its "turn-over" are 10~100 times for each radical initiation step leading to increasing yields of 6 with increasing the ratio

Table 2. Homolytic reactions of variable t-butylisocyaide^t 7 and cumene with t-butylperoxide (TBP)^t or benzoylperoxide (BP)^t in chlorobenzene.

$$t-\text{BuO} \cdot - \begin{array}{c} & \text{B} & \text{A} \\ & & \text{T} \\ & & \text{Bu} \\ & & \text{N} \\ & & \text{Cumene} \\ & & \text{k_0, (9)} \\ & & \text{t-BuOH + Cumyl radical} \end{array}$$

$$(8)$$

$$Ph - \begin{vmatrix} \frac{7}{k_{10s}, (10a)} \rightarrow t - Bu - N = \hat{C} - Ph & \longrightarrow PhCN + t - Bu - PhC$$

$$t-\text{BuN} \equiv \text{C} + t-\text{Bu} \cdot \frac{11}{(12a)} \rightarrow t-\text{BuN} = \text{C}-\text{Bu-t} \cdot \frac{(12b)}{(12b)} \rightarrow t-\text{BuCN} + t-\text{Bu} \cdot \frac{1}{(12b)}$$

$$7 \qquad 2a \qquad 6 \qquad (12)$$

No.	Radical sources	7	Cume _M_		remp°K-	8 ^d	94		10* m.\/	11'		6	
		a	b	a/b	Temp	с	đ	c/d	e	f	e/f	g .	
1.	TBP	(0.1 M)	2. 02	4.94	0.41	398	0.94	1.87	0.50	_		-	62
2.	TBP	(0.1 M)	2.38	1.51	1.73	398	1.73	1.40	1.23	_	-		249
3.	TBP	(0.1 M)	2. 24	2, 75	2.06	398	2.06	0.83	2.48	_	_	-	547
4.	BP	$(5 \mathrm{m} M)$	1.50	5.92	0.25	373	_	_	_	4.70	2.50	1.88	97
5.	BP	$(5\mathrm{m}M)$	2.03	5. 55	0.37	373	_			4.90	1.68	2.92	149
6.	BP	$(5 \mathrm{m} M)$	2, 53	5.09	0.50	373	_	_	_	5. 34	1, 53	3.49	222

For quantitative analysis of isonitriles by VPC, we recommend glass tubing as column material. The poor response of isonitries with metal tubing was ascribed to a irreversible absorption to the metal surface ^{12,13}. ^bTBP has decomposed 2.8 % after 15 min at 398 °K. ^cBP has decomposed over 99 % after 3.5 HR at 373 °K. ^dProduct analyses were carried out by VPC using 11 ft, 20 % TCEP on chromosorb P column at 60 °C, inj. port 100 °C. TBP dis not decompose significantly during the VPC analysis under the condition. Toluene was added to the samples before injection as an internal standard. ^cProduct analyses were carried out by VPC using 12 ft, 20 % TCEP on chromosorb P column at 50 °C for benzene, at 100 °C for pivalonitrile andat 150 °C for benzenitrile.

of [7]/[cumene]. Qualitatively, the turn over factor increases with increasing isonitrile concentration which is constistent with the radical chain process. Eq. (12) is well contrasted with eq. (5) and (6) which do not constitute chain process.

Addition of Silyl Radical to 7. Mercury sensitized gas phase phase photolysis of a mixture of trimethylsilane (TMS) and 7 was carried out in a Quartz cell. ¹⁵ After one hour of photolysis, IR spectrum of the reaction mixture showed formation of trimethylsilyl cyanide (TMSC) as is shown in *Schem 3*.

Photolytically generated imidoyl radical t-Bu-N= \dot{C} -Si(Et)₃ was observed by ESR⁶, which

rapidly collapsed to Et₃SiCN and t-butyl radicaleven at low temperature.

Attempted Homolytic α -Addition of an Alkylhalide to t-Butyl Isocyanide 7. Various polar reagents have been observed to add to the divalent carbon atom of isonitriles. ¹⁴ However the α -addition of a carbon-halogen bond to an isonitrile has not yet been reported.

The addition of t-butyl chloride to 7 under radical conditions was attempted. A mixture of t-butylchloride and 7 (t-BuCl/7 = 2) was heated at 75 $^{\circ}$ C in the presence of decomposing azo-bisisobutyronitrile (AIBN). After seven half-lives of the initiator, the mixture was analyzed by NMR spectroscopy, which showed

$$Hg(Vapor) \xrightarrow{2537A^{\circ}} Hg^{*}(3p)$$
 (13)

$$(CH_3)_3SiH \xrightarrow{Hg^*} \rightarrow (CH_3)_3Si \cdot + H \cdot$$
 (14)

$$t\text{-BuN} \equiv C \xrightarrow{\text{(CH3)}_{s}\text{Si} \cdot } t\text{-Bu-N} = C\text{-Si}(\text{CH}_{3})_{3} \xrightarrow{\text{(CH}_{3})_{3}\text{SiCN}} + t\text{-Bu} \cdot \tag{15}$$

$$(CH_3)_3 SiH \xrightarrow{t-Bu} \rightarrow (CH_3)_3 Si \cdot + t-BuH$$
 (16)
Scheme 3.

$$t-\text{Bu}\text{N}\equiv\text{C}-\frac{t-\text{Bu}}{7}\longrightarrow t-\text{Bu}-\text{N}=\dot{\text{C}}-\text{Bu}-t$$

$$t-\text{Bu}-\text{CN} + t-\text{Bu}$$

$$t-\text{Bu}-\text{CN} + t-\text{Bu}$$

$$t-\text{Bu}-\text{CN} + t-\text{Bu}$$

$$t-\text{Bu}-\text{Cl}$$

$$t-\text{Bu}-\text{N}=\text{C}$$

$$t-\text{Bu}-\text{N}=\text{Cl}$$

Scheme 4.

the formation of pivalonitrile (40.8 % based on the starting 7) but no sign of the hoped-for imidoyl chloride 13. The mechanism might be shown in *Scheme* 4.

The absence of imidoyl chloride 13 may be explained by the likelihood that the formation of an imidoyl C-Cl bond is energetically unfavorable because of its weak bond strength which may be comparable to the C-Cl bond of an acid chloride.

β-Cleavage vs. Atom Transfer Reaction. β-Cleavage and atom transfer are the two competing reactions by which imidoyl radicals would be stabilized. The participation of the reactions may be determined by various factors, e.g. temperature, amount of internal energy possessed by the radical¹⁶, relative stabilities of incipient and departing radicals and so on.

Increase of reaction temperature and internal energy will favor the β -cleavage. The cleavage would be also facilitated when departing radical is more stable than the incipient one.

Imidoyl radical 2 may undergo β -cleavage in two different directions. One is the cyanide transfer reaction, e.g. eq. (2) and the other is "so-called" normal β -cleavage, e.g. eq. (3). Since cyanide transfer involves the isomerza-

tion of less stable isonitrile to more stable nitrile, the reaction is also facilitated by this facor, which explains why eq. (12) makes a very efficient chain process.

Pritchard and Shaw² estimated reaction (19a) and (19b) to be 5~10 kcal exothermic, respectively.

$$CH_3-N \equiv C + \cdot CH_3 \xrightarrow{(19a)} CH_3-N = \hat{C}-CH_3$$

$$\xrightarrow{(19b)} \cdot CH_3 + NC-CH_3$$
(19)

2a may be generated by either the addition of t-butyl radical to 7, eq. (1a) or hydrogen abstraction from imine, eq. (1b). While the ESR spectrum of 2a was not detected in the former case⁶, it has been reported with the latter case. ⁵ Generation of 2a via eq. (1a) would be exothermic so that 2a should possess some internal energy which facilitates the fragmentation of 2a thereby keeping the concentration of 2a very low (below EPR detectability).

Cyanide transfer is one of the characteristic reactions of imidoyl radicals, 2a, 2c and 2d which would be rather stabilized by the cleavage than by atom transfer reaction.

Imidoyl radicals would be generated by addition of alkoxy or thiyl radical³ to alkyl isonitriles. The resulting imidoyl radical may

be stabilized by either the "so-called" normal β -cleavage or the hydrogen transfer depending upon stabilities of departing radicals.

Imidoyl radicals, 2b undergoes exclusively the β -cleavage to give 8 and t-butyl radical rather than hydrogen transfer reaction. The stabilities of departing radicals are well reflected on the direction of the cleavage.

CONCLUSION

The capacity of t-butylisonitrile 7 as the radical scavenger may be well compared with that of cumene.

The key intermediate imidoyl radicals may be stabilized by either β -cleavage or atom transfer reactions. β -Cleavage would be further classified as cyanaide transfer and "so-called" normal β -cleavage reactions. Both β -cleavage reactions often make efficient radical chain isomerizations.

EXPERIMENT

Instruments. Infrared spectra were recorded either on a Perkin-Elmer infrared spectro-photometer 137 or 337 using 6.24 band of a polystyrene film as calibration peak. Their cells are 0.15 mm in path length unless otherwise indicated.

All the nuclear magnetic resonance (NMR) spectra were taken on either a Varian Associates A-60 or a T-60 spectrometer with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million downfield from TMS.

Melting point determinations were made with an Electrothermal melting point apparatus and were uncorrected.

Reagents. Cumene: Matheson Coleman & Bell reagent was shaken with concentrated H₂SO₄ until no further yellow coloration occurred. It was then washed with water and

aqueous sodium bicarbonate 3 times, respectively, dried over MgSO₄, and distilled. Only the centre cut was collected and stored under nitrogen in darkness.

t-Butyl Peroxide: Practical grade (Matheson Coleman & Bell) was fractionally distilled with Vigreux column under water aspirator pressure and kept in refrigerator.

Benzoyl Peroxide: It (Mallinckrodt Chemical Co.) was recrystallized in ether-petroleum ether solvent.

t-Buyl Isocyanide 717. In a 500 ml roundbottomed flask equipped with a magnetic stirring bar and reflux condenser was placed 40 g of t-butyl formamide (0.398 mole), 179g of pyridine (2.28 mole) and 85 ml of pentane. The mixture was immersed in an ice-bath to maintain the temperature 0~5°C. To this mixture, was added dropwise 69.6g of phosphorus oxychloride (0.228 mole) and the mixture was stirred for one hour. Then the mixture was warmed to 60 °C for 15min and cooled again to 0~5°C with an ice-bath. The reaction mixture was poured into 200 ml of ice water and the organic layer was extracted with pentane several times. The pentane extract was washed with water more than five times to eliminate the remaining pyridine in the pentane layer (this procedure is very important for the complete removal of pyridine). Then, the pentane layer was dried over anhydrous sodium sulfate and subject to fractional distillation to give 19.3 g of pure 7, (58 % yield) b. p. 92~93°C/760 mmHg. NMR of neat 7 shows a 1:1:1 triplet peak at 1.17 δ with $J^3(N-H)$ of 2.4 Hz. IR(neat) $v = 2130 \text{cm}^{-1}(\text{RN} \equiv \text{C})$.

N-Neopentylidene-t-butyl Amine, 3a^{7,8}. The mixture of freshly distilled pivalaldehyde (5. 70 g, 66.2 mmole) and t-butyl amine (5. 7 g, 78 mmole) was stirred for 1.5 hr at room temperature. Molecular sieve was added and the

mixture was left overnight at room temperature without stirring. After filtration of the molecular sieve the mixture was fractionally distilled under nitrogen to give 4.6g of colorless liquid (50 % yeild) at boiling point of $117\sim120$ °C. The sample showed satisfactory NMR and IR spectra as shown below. Since compound 3a is easily hydrolyzed even by the moisture in the air, it should be used right after its purification and stored in degassed, sealed tube. IR (neat): $1665 \, \text{cm}^{-1}$ (C=N), $1 \, \text{H}$ NMR (neat): 1.12(S, 9H), 1.02(S, 9H),

Hexamethyl Siloxane. Trimethylchlorosilane (108.6 g, 1.0 mole) was dissolved in 100 ml of water. The reaction mixture became warm and was stirred for 6 hrs. The organic layer was extracted with ether three times and the ether layer was dried over anhydrous magnesium sulfate. The ether was evaporated by rotary evaporator to give the crude hexamethyl siloxane. The crude product was fractionally distilled with a Vigreux column and the middle portion (b. p 97~98 °C) was collected to give 50.0 g of clear liquid (yield 31.0%)

Trimethyl Bromosilane¹⁸. Phosphorus tribromide (141 g, 0.52 mole) was added slowly to hexamethyl siloxane (53 g, 0.33 mole) and the mixture was stirred at room temperature for 3 hrs and refluxed at 120 °C for 1.5 hr under nitrogen. During the reflux (after 50 min) phosphorus began to precipitate. The resulting reaction mixture was distilled in situ to give the crude trimethylbromosilane (b. p range: $80\sim90$ °C), which was fractionally distilled under nitrogen to give 34g of pure product (yield: 67.0%) with b. p $78\sim79$ °C/760 mmg. IR: identical with authentic sample. ¹H NMR (neat): 0.57δ (S, 9H)

Trimethyl (iso)* Cyanosilane 12¹⁹. Trimethylbromosilane (15.3 g, 0.10 mole) and silver cyanide** (19.0 g, 0.142 mole) were mixed.

The mixture became warm and the white silver cyanide turned to light yellow. The mixture was refluxed at 110 °C under nitrogen for 40 min and in situ distilled to give the crude product.

This was fractionally distilled to give 3.6 g of colorless liquid (yield: 36.4 %) with b. p of 114~116 °C (reported: 114~117 °C)²⁰.

¹H NMR(neat) 0.33 δ (S, 9 H), IR(neat) v 2170 cm⁻¹(intense, SiC \equiv N), v 2100cm⁻¹ (weak, Si-N \equiv C).

Thermolysis of t-Butyl Isocyanide 7 with Different Ratios of Cumene in the Presence of Decomposing Di-t-Butyl Peroxide (TBP).

Samples of compound 7, cumene and TBP were weighed into a $10\,\mathrm{ml}$ volumetric flask for desired concentration as is shown in Table 2. Toluene was added as an internal standard and chlorobenzene was added to the mark. The flask was shaken well to give a homogeneous solution. The solution was divided into several $13\times100\,\mathrm{mm}$ Pyrex tubes constricted approximately 2 cm from the open and for easy sealing. The solution was then degassed 2 times at dry ice-acetone temperature to $100\sim50\,\mu\mathrm{Hg}$ pressure and sealed. After warming to room temperature, the tubes were placed in a wire basket and immersed in an oil bath regulated at $125\pm0.3\,^{\circ}\mathrm{C}$.

The tubes were kept in the bath for 15 min

It has been generally accepted that the nitrile isomer is in labile equilibrium with a small amount (abot 10 %) of isonitrile isomer. ^{19,20} However, variable temperature infrared study²¹ showed a value of ΔH° =4.02±0.04 kcal/mole for the reaction below and the mole fraction of isonitrile in thle izuid to be only 0.0015±0.0005 at 25 °C

 $⁽CH_3)_3Si-C\equiv N \leftarrow ------ (CH_3)_3Si-N\equiv C$

^{**}Since silver cyanide is photosensitive, all the reactions were carried out under darkness. Silver cyanide was prepared by reaction of potassium cyanide and silver nitrate under darkness.

to give 2~3% decomposition of TBP and then removed, quenched in ice water and opened for analyses.

Thermolysis of t-Butyl Isocyanide 7 with Different Ratios of Cumene in the Presence of Decomposing Benzoyl Peroxide(BP). Samples of compound 7 and cumene were weighed into a 5 ml volumetric flask and chlorobenzene was added to the mark giving the concentrations shown in Table 2. Into a 2 ml volumetric flask was weighed recrystallized BP (2.4 mg, 0.005 M) and this was filled with the previously prepared solution to the mark. The flask was shaken until a homogeneous solution was obtained. The solution was divided into several 13 ×100 mm Pyrex tubes and degassed two times at liquid nitrogen temderature to 100~50 μHg pressure and sealed. After warming to room temperature, they were thermolyzed in oil bath at 100±0.3°C for 3.5 hrs corresponding to 99 decomposition of BP. They were then removed, cooled to room temperature and opened for analyses.

Thermolysis of N-Neopentilidene-t-butyl Amine 3a with Di-t-Butyl Peroxide (TBP). Samples of compound 3a (2.115 g, 1.5 M) and TBP (0.146 g, 0.1 M) were weighed into a 10 ml volumetric flask which was filled with chlorobenzene to the mark. The solution was divided into Pyrex ampoules, which were degassed and thermolyzed at 125 °C. Reaction samples were periodically taken out and quenched in ice-water (20, 40, 70, 120, and 170 min) and analyzed on the TCEP column at 60 °C.

Photolysis of Trimethylsilane with t-Butyl Isocyanide 7. Gas samples of trimethylsilane (3.80 torr) and compound 7 (2.30 torr) were introduced into a Quartz cell by vacuum line techniques with one drop of mercury as sensitizer. The mixture was then photolyzed using a high pressure mercury lamp for one hour.

The resulting gas mixture was introduced into an IR gas cell and IR was taken by Beckmann IR 20-A, which was compared with that of authentic trimethyl(iso)cyanosilane 12.

Homolytic α-Adddition of t-Butyl Chloride to t-Butyl Isocyanide 7. Samples of compound 7 (2.075 g, 25 mmole), t-butyl chloride (4.630 g, 50 mmole) and AIBN (0.2 g, 2.5 mmole) were dissolved in 5 ml of benzene and flushed with nitrogen. The mixture was heated at 75 °C for 22 hrs under nitrogen and an NMR spectrum was taken for the resulting reaction mixture, which showed the formation of pivalonitrile.

Products Analyses. Analyses of the products of the thermolyses were carried out by vapor phase chromatography using an A-90-P model Aerograph with thermal conductivity detector. A12'×1/4" 20 % TCEP on chromsorb P was with a helium flow rate of 1ml/sec.

ACKNOWLEDGEMENT

The author warmyl thanks Professor L. A. Singer for initiating the ressearch and Department of Chemistry, University of Southern California for their generous support of this work.

REFERENCES

- (a) For a review see T. Saegusa and Y. i Ito in
 "Isonitrile Chemistry", Ed. I. Ugi, Academic Press,
 New York, 1971; (b) In accordance with generally
 accepted usage, the term isonitrile is used for the
 general class of compounds, whereas the term
 isocyanide is used for specific designations (e.g.,
 ethyl isocyande or alkyl isocyanide).
- D. H. Shaw and H. O. Pritchard, Can. J. of Chem., 45, 2749 (1967).
- T. Saegusa et al., J. Org. Chem., 35, 2118 (1970).
- 4. R. N. Haszeldine et al., Tett. Lett., 3699 (1972),
- 5. W. C. Danen and C. T. west, J. Amer. Chem.

- Soc., 95, 6872 (1973).
- P. M. Blum and B. P. Roberts, J. C. S. Chem. Comm., 535 (1976).
- 7. R. Bonnett, J. Chem. Soc., 3213 (1965).
- J. C. Sheehan and J. H. Beeson, J. Amer. Chem. Soc., 89, 362 (1967).
- M. Szwarc and J. W. Taylor, Trans. Far. Soc., 47, 1293 (1951).
- L. A. Singer and S. S. Kim, Tett. Lett., 861 (1974).
- 11. S. S. Kim, Tett. Lett., 2741 (1977).
- S. H. Beuer et al., J. Amer. Chem. Soc., 86, 1488 (1964).
- A. G. Kelso and A. B. Lacey, J. Chromatog.,
 18, 156 (1965).
- The author is grateful to Professor D. D. Tanner for pointing out the direction B.
- 15. The vacuum line should maintain a high vacuum

- $(\sim 5 \times 10^{-6} torr)$ for the reaction. At $\sim 10^{-3} torr$, the reaction did not take place at all.
- "Mechanism and Products During the Homolytic Addition of CCl₄ and Cl₃CBr to β-Halostyrenes",
 S. S. Kim, submitted for publication.
- (a) I. Ugi and R. Meyer., Angew. Chem., 70, 702 (1958);
 (b) J. J. Casanova, Jr. et al., J. Org. Chem., 31, 3473 (1968).
- (a) W. F. Gilliam, R. N. Meals and R. O. Sauer,
 J. Amer. Chem. Soc., 68, 1161 (1946); (b) P.
 A. McCusker and E. L. Reilly, J. Amer. Cher.
 Chem. Soc., 75, 1583 (1952).
- C. Eaborn, J. Chem. Soc., 2755 (1949) and 3077 (1950).
- J. J. Macbrid, Jr. and H. C. Beachell, J. Amer. Chem. Soc., 74, 5247 (1962).
- M. R. Booth and S. G. Frankiss, Spectrochimia Acta., 264, 859 (1970).