Cationic Isomerization and Oligomerization of Isocyanide

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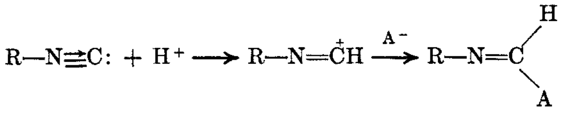
Cationic reactions of isocyanide which have hitherto been studied are mostly caused by Brønsted acids. As to the Lewis acid catalyzed reaction, the cationic polymerization of isocyanide, producing an insoluble and infusible polymer, has been reported. The present study has shown that the cationic polymerization by Lewis acid catalyst is limited to the isocyanides of primary and secondary alkyls, and that tertiary alkyl isocyanide is converted by Lewis acid into the corresponding cyanide and oligomers.

In general, cationic reactions[1] are initiated by the electrophilic addition of a cationic species to isocyanide generating an imidoyl cation **1** (eq 1). The courses of

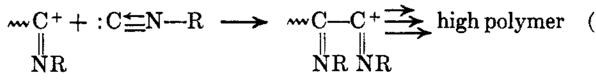
$$\mathrm{R{-}N{\overset{\rightarrow}{\equiv}}C\colon + R'^+ \longrightarrow \underset{\mathbf{1}}{R{-}N{=}\overset{+}{C}{-}R'}} \tag{1}$$

various cationic reactions of isocyanide are explained by a key intermediate of **1**. In the reaction of isocyanide with a Brønsted acid, formimidoyl cation **2** is combined with an anion of the acid to form the α,α addition product **3**. The cationic polymerization of isocyanide



$$\mathrm{R{-}N{\overset{\rightarrow}{\equiv}}C\colon + H^+ \longrightarrow \underset{\mathbf{2}}{R{-}N{=}\overset{+}{C}H} \xrightarrow{A^-} \underset{\mathbf{3}}{R{-}N{=}C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown A}}} \tag{2}$$

may be understood by the successive nucleophilic addition of isocyanide to the growing chain end having the imidoyl cation structure. The decomposition tendency



$$\mathrm{{\sim}\underset{\substack{\|\\ NR}}{C^+} + \colon C{\overset{\leftarrow}{\equiv}}N{-}R \longrightarrow {\sim}\underset{\substack{\|\\ NR}}{C}{-}\underset{\substack{\|\\ NR}}{C^+} \rightrightarrows high\ polymer} \tag{3}$$

of **1** through a mode of β scission (eq 4) will be strong when the alkyl group attached to nitrogen in **1** is a good leaving one as an alkyl cation. The combination of

$$\mathbf{1} \rightleftarrows \mathrm{R'C{\equiv}N + R^+} \tag{4}$$

two elementary processes, the electrophilic addition of the tertiary alkyl cation to isocyanide and the subsequent β scission of the imidoyl cation, constitutes the cationic isomerization of tertiary alkyl isocyanide to the corresponding cyanide. In the cationic polymerization, the decomposition of β scission of the imidoyl cation at the growing end is the so-called "chain transfer." The cationic oligomerization of isocyanide corresponds to a kind of polymerization with frequent chain transfer according to eq 4. The isomerization and oligomerization of isocyanide are thus related to each other. However, the courses of the cationic reactions of isocyanide caused by Lewis acid catalyst are somewhat complicated by the fact that the isomerization product of cyanide functions as another nucleophile and competes with isocyanide in the reaction with alkyl cation. For example, the reverse reaction of eq 4 is a nucleophilic addition of cyanide to alkyl cation, which is known as the Ritter reaction.

In this paper, the whole course of the cationic reactions of tertiary alkyl isocyanide is first described and then these reactions are discussed in relation to several cationic reactions, *e.g.*, the von Braun reaction, Ritter reaction, and Vilsmeier reaction. The results of the present study provide a general scope of the cationic reactions of isocyanide.

Results and Discussion

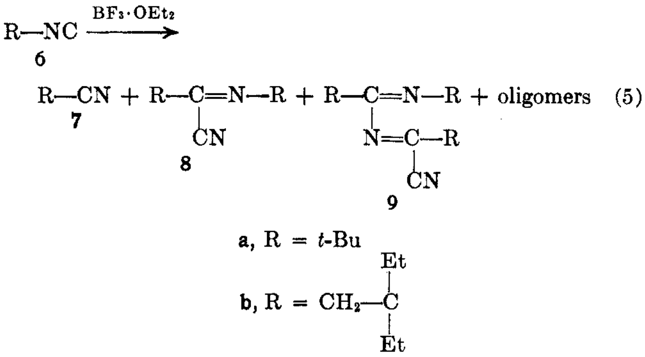
When cyclohexyl and isopropyl isocyanides were treated by a catalytic amount of Lewis acid, only insoluble and infusible polymers were produced in almost quantitative yields (eq 3, R = c-C_6H_{11} and i-C_3H_7). This result was in accord with the work of Hagiwara, *et al.*[2] In the treatment of tertiary alkyl isocyanide (**6**) with $BF_3\cdot OEt_2$, however, the tertiary alkyl cyanide (**7**), imidoyl cyanide (**8**), (N-imidoyl)imidoyl cyanide (**9**), and a mixture of oligomers were produced. Among three products, **7** is the isomer of isocyanide, and **8** and **9** may be regarded as being derived by dimerization and trimerization along with isomerization, respectively.

TABLE I
REACTION OF TERTIARY ALKYL ISOCYANIDE WITH $BF_3\cdot OEt_2$ CATALYST[a]

Isocyanide	Reaction temp, °C	Products, %[b] 7	8	9
6a	0	28	45	[c]
	rt[d]	49	16	2
	0[e]	4	67	[c]
6b	0	50	8	[c]
	rt	74	3	[c]

[a] 15 mol % of $BF_3\cdot OEt_2$ was used as catalyst. [b] Determined by glpc analysis. [c] Not determined. [d] Room temperature. [e] 50 mol % of t-BuCN was added to the reaction system.

Table I shows the cationic reactions of t-butyl isocyanide (**6a**) and of 3-methylpentyl 3-isocyanide (**6b**) caused by $BF_3\cdot OEt_2$



$$\underset{\mathbf{6}}{\mathrm{R{-}NC}} \xrightarrow{\mathrm{BF_3\cdot OEt_2}} \underset{\mathbf{7}}{\mathrm{R{-}CN}} + \underset{\mathbf{8}}{\mathrm{R{-}\underset{\substack{|\\ CN}}{C}{=}N{-}R}} + \underset{\mathbf{9}}{\mathrm{R{-}\underset{\substack{|\\ N=\underset{\substack{|\\ CN}}{C}-R}}{C}{=}N{-}R}} + \text{oligomers} \tag{5}$$

$$\mathbf{a},\ \mathrm{R} = t\text{-}\mathrm{Bu} \qquad \mathbf{b},\ \mathrm{R} = \mathrm{CH_2{-}\overset{\substack{Et\\ |}}{\underset{\substack{|\\ Et}}{C}}}$$

The reaction proceeds smoothly at temperatures as low as 0°. The relative amount of each product was

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(1) I. Ugi, *Angew. Chem.*, **74**, 9 (1962).

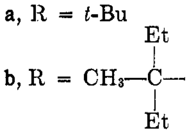
(2) Y. Yamamoto, T. Takizawa, and N. Hagiwara, *Nippon Kagaku Zasshi*, **87**, 1355 (1966).

affected by the reaction temperature; *i.e.*, in the reaction of **6a**, the formation of **8a** is favored at 0°, whereas that of **7a** is favorable at room temperature. Interestingly, the addition of **7a** to the reaction system increased the yield of **8a**. This finding has an important bearing upon the reaction mechanism which will be discussed later. Besides $BF_3 \cdot OEt_2$, $SnCl_4$ also induced the isomerizations of **6a** and **6b** to produce **7a** and **7b**, respectively, in decreased yields. $TiCl_4$ and $AlCl_3$ formed the irrespective metal–isocyanide complex and they did not induce the above cationic reactions.

The structures of **8** and **9** were established by ir and nmr spectra and the HCl hydrolysis product as well as elemental analysis. The hydrolyses of **8** and **9** with a warm HCl aqueous solution gave the corresponding acyl cyanide (**10**) and amide (**11a**), respectively. When

$$\mathbf{8} \xrightarrow{\text{aqueous HCl}} \underset{\mathbf{10}}{\mathrm{RCOCN}} \qquad (7)$$

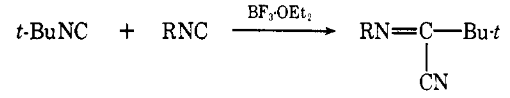
a, R = *t*-Bu



$$\text{b, R} = \mathrm{CH_3{-}C(Et)_2{-}}$$

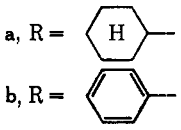
$$\mathbf{9a} \xrightarrow{\text{aqueous HCl}} \underset{\mathbf{11a}}{t\text{-}\mathrm{BuCONHBu}\text{-}t} \qquad (8)$$

a mixture of **6a** and another isocyanide was treated with $BF_3 \cdot OEt_2$, the imidoyl cyanide **12** which could be regarded as an isomerized codimer of the two isocyanides was produced. It is of interest that the $BF_3 \cdot OEt_2$ catalyzed reactions of primary and secondary alkyl isocyanides produce only the polymers of isocyanides, but the reactions carried out in the presence of tertiary alkyl isocyanide give the codimers. In the $BF_3 \cdot OEt_2$ catalyzed reaction of a mixture of cyclohexyl isocyanide and **6a**, the petroleum ether soluble oligomer of isocyanide (mol wt 430) was produced in addition to **12a**. Furthermore, a small amount of N-cyclohexylpivaloamide (**13**) was also isolated in the reaction mixture after treated with dilute alkaline. The formation of **13** is reasonably ascribed to the presence of the imidoyl cation complex **14** which exists in the reaction system. In the combination of **6a** and **6b**, which were both tertiary alkyl isocyanides, two isomeric codimers (**15** and **16**)



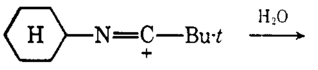
$$t\text{-}\mathrm{BuNC} + \mathrm{RNC} \xrightarrow{BF_3 \cdot OEt_2} \mathrm{RN{=}C(CN){-}Bu}\text{-}t \qquad (9)$$

12

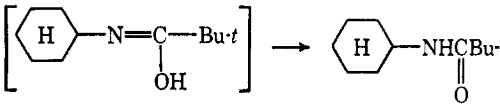


a, R =

b, R =

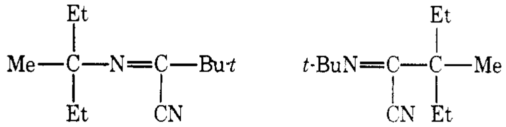


14



(10)

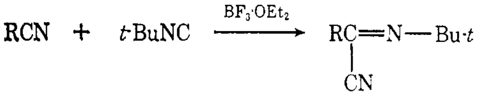
13



15 **16**

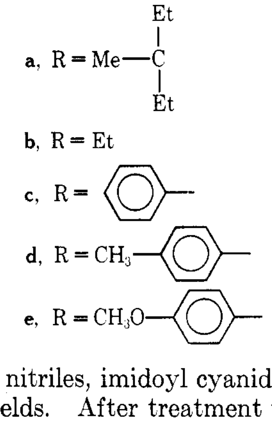
were produced in addition to **8a** and **8b**. As will be discussed in the section of reaction mechanism, **15** is produced also in the cationic reaction of **6a** with 3-methylpentyl 3-cyanide (hereafter abbreviated to *t*-hexyl cyanide or *t*-HexCN).

The Lewis acid catalyzed reaction of tertiary alkyl isocyanide with nitrile was then studied. This reaction is significant in two aspects. The first is a mechanistic one; *i.e.*, tertiary alkyl isocyanide is isomerized by Lewis acid into the corresponding cyanide (nitrile) which is also a potent nucleophile and competes with isocyanide in the reaction with alkyl cation. The second is that the cationic reaction of this combination provides new cationic reactions of isocyanide.[3-5] The $BF_3 \cdot OEt_2$ catalyzed reactions of **6a** with several nitriles including aliphatic and aromatic ones are shown in Table II. The reaction was carried out in methylene chloride at room temperature. Imidoyl cyanides (**18**) were produced along with the isomerized product **7a** and the isomerized dimer **8a**.



$$\mathrm{RCN} + t\text{-}\mathrm{BuNC} \xrightarrow{BF_3 \cdot OEt_2} \mathrm{RC(CN){=}N{-}Bu}\text{-}t \qquad (11)$$

17 **18**



a, R = Me—C(Et)₂—

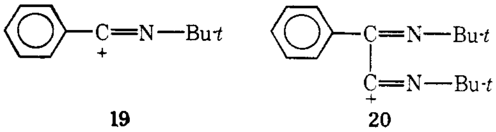
b, R = Et

c, R =

d, R = CH₃—

e, R = CH₃O—

With aromatic nitriles, imidoyl cyanides **18** were obtained in good yields. After treatment with dilute alkaline, small amounts of N-*t*-butyl benzamide and N-*t*-butyl-2-phenylglyoxylamide were isolated. These two products are taken to indicate the presence of the complexes of the two cationic species, **19** and **20**. These two species are important in the mechanism consideration.



19 **20**

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[3] T. Saegusa, N. Taka-ishi, and H. Fujii, *J. Polym. Sci., Part B*, **5**, 779 (1967).

[4] T. Saegusa, N. Taka-ishi, and H. Fujii, *Tetrahedron*, **24**, 3795 (1968).

[5] T. Saegusa, N. Taka-ishi, I. Tamura, and H. Fujii, *J. Org. Chem.*, in press.

DIAGRAM I

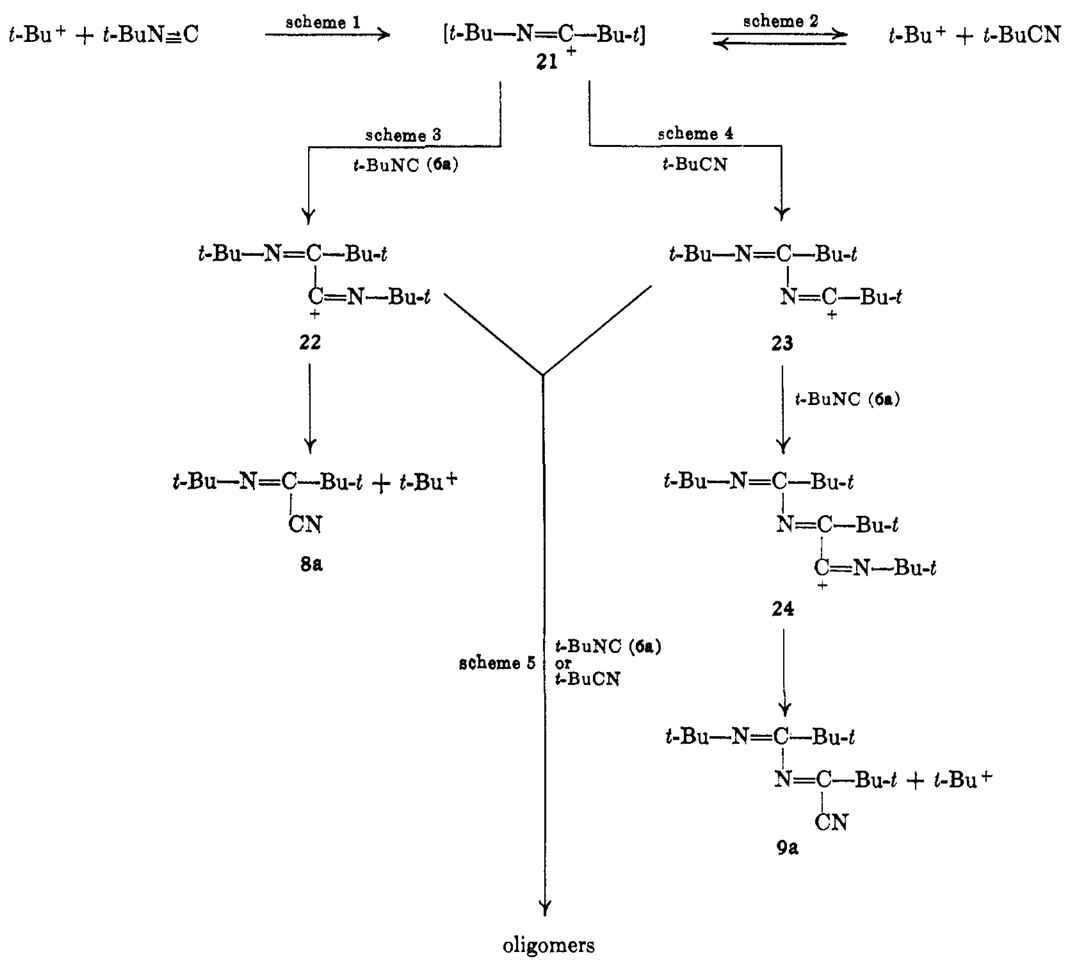
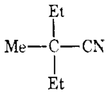
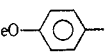
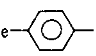
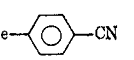
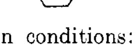
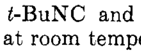


TABLE II
REACTION OF NITRILES WITH t-BUTYL ISOCYANIDE[a]

t-BuNC, mmol	RCN, mmol		BF₃·OEt₂, mmol	Solvent CH₂Cl₂, ml	Yield of 12, %
10	EtCN	10	1.5	10	4
10	 $Me-C(Et)_2-CN$	4.6	1.5	10	12
10		10	1	10	37
10		10	10	20	50[b]
5		5	0.75	5	37
10		10	1	10	40
20		10	1.5	10	50

[a] Reaction conditions: $BF_3 \cdot OEt_2$ was added dropwise to a mixture of t-BuNC and nitrile in CH_2Cl_2. The reaction was carried out at room temperature for 1 day. [b] t-Butyl isocyanide was added dropwise to a mixture of benzonitrile and $BF_3 \cdot OEt_2$ in CH_2Cl_2.

Mechanism

The reactions of the **6a** caused by Lewis acid catalyst are schematized in Diagram I which explains all the reaction products. Every scheme is initiated by t-butyl cation and finally results in the regeneration of t-butyl cation. The formation of isobutylene during the reaction was frequently observed, which is taken to support the schemes involving t-butyl cation complex as the reaction carrier.

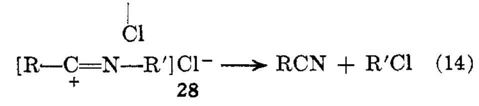
As to the initial generation of t-butyl cation complex, two possibilities may be presented. The first is the direct interaction between **6a** and a Lewis acid catalyst, e.g., $BF_3 \cdot OEt_2$ (eq 12). The second is the participation

$$\begin{gathered} t\text{-BuNC} + BF_3 \cdot OEt_2 \rightleftharpoons (t\text{-BuNC} \rightarrow BF_3) + Et_2O \\ (t\text{-BuNC} \rightarrow BF_3) \longrightarrow t\text{-Bu}^+[BF_3 \cdot CN]^- \end{gathered} \tag{12}$$

of a small amount of water of an impurity to produce protonic acid complex **25**. The electrophilic addition of **25** to **6a** gives the formimidoyl cation complex **26** whose decomposition generates the t-butyl cation complex **27** and hydrogen cyanide (eq 13). The conversion

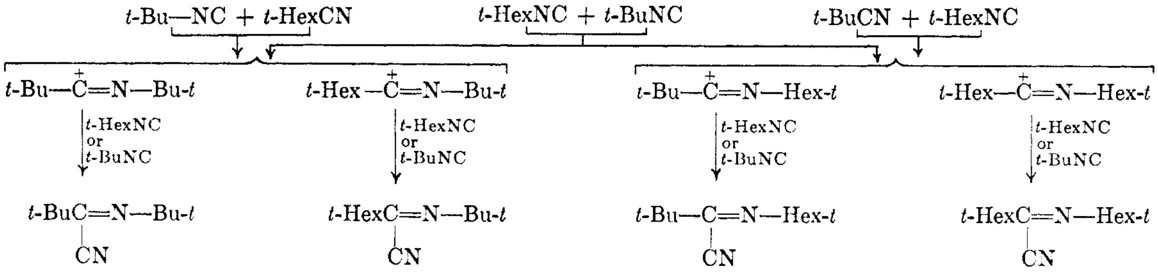
$$\begin{gathered} BF_3 \cdot OEt_2 + H_2O \rightleftharpoons \underset{\mathbf{25}}{H^+[BF_3OH]^-} + Et_2O \\ H^+[BF_3OH]^- + t\text{-BuNC} \longrightarrow \underset{\mathbf{26}}{t\text{-BuN}{=}C^+H[BF_3OH]^-} \longrightarrow \\ \underset{\mathbf{27}}{t\text{-Bu}^+[BF_3OH]^-} + HCN \end{gathered} \tag{13}$$

of **26** into **27** resembles the decomposition of the imidoyl cation **28** in the von Braun reaction, in which N-tertiary



$$\begin{gathered} RCONHR' \xrightarrow{PCl_5 \text{ or } SOCl_2} R-\underset{Cl}{\underset{|}{C}}=N-R' \longrightarrow \\ \underset{\mathbf{28}}{[R-\overset{}{\underset{+}{C}}=N-R']Cl^-} \longrightarrow RCN + R'Cl \end{gathered} \tag{14}$$

DIAGRAM II



8a **15** **16** **8b**

t-HexNC = 3-methylpentyl 3-isocyanide
t-HexCN = 3-methylpentyl 3-cyanide

amide is treated with PCl_5 or $SOCl_2$ to produce alkyl chloride and nitrile.[6]

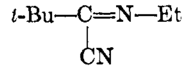
In Diagram I, t-butyl cation first adds to **6a** to give imidoyl cation (**21**) (scheme 1), whose decomposition into t-butyl cyanide and t-butyl cation (scheme 2) constitutes the isomerization reaction. Scheme 2 is reversible, and the reverse reaction is known as an elementary process of the Ritter reaction.[7] The imidoyl cation **21** reacts with the second molecule of **6a** to produce a new imidoyl cation (**22**), which decomposes to produce **8a** and t-butyl cation (scheme 3). The imidoyl cation (**21**) also reacts with t-butyl cyanide to give an imidoyl cation (**23**) which is isomeric with **22**. A subsequent reaction of **22** with **6a** produces **24**, which on decomposition gives **9a** and t-butyl cation (scheme 4). Successive nucleophilic additions of **6a** and t-butyl cyanide to the cationic species such as **21**, **22**, **23**, and **24** will be interrupted by the decomposition at the growing end having the imidoyl cation structure, which corresponds to the oligomerization. **6a** is a monomer having a strong tendency to the so-called "chain transfer" reaction. In the present reaction, a mixture of soluble oligomers of **6a** having low molecular weights was produced in low yields.

All the above schemes are understood as being composed of combinations of three elementary reactions, *i.e.*, the additions of t-butyl and imidoyl cations to **6a**, the additions of t-butyl and imidoyl cations to t-butyl cyanide, and the decompositions of N-t-butylimidoyl cations into the nitriles and t-butyl cation. The second elementary reaction is the electrophilic addition of carbonium ion to cyanide (nitrile), which is the isomerization product. This has been demonstrated clearly in the $BF_3 \cdot OEt_2$ catalyzed reaction of **6a** with benzonitrile, where **18c** and N-t-butylbenzamide were produced. Especially, the latter product is a direct support of the complex of **19** which is formed by the addition of t-butyl cation to benzonitrile. Moreover, it is shown in Table I that the addition of t-butyl cyanide to the system of the $BF_3 \cdot OEt_2$ catalyzed reaction of **6a** increases the relative yield of **8a**. This finding supports the view that scheme 2 is reversible.

The $BF_3 \cdot OEt_2$ catalyzed reaction of a mixture of **6a** and **6b**, two tertiary alkyl isocyanides, gave four imidoyl cyanides, **8a**, **8b**, **15**, and **16**. On the other hand, the reaction of a mixture of **6a** and 3-methylpentyl 3-cyanide gave **8a** and **15**, and the combination of **6b** and t-butyl cyanide gave **8b** and **16** (see Diagram II). These results indicates that the carbonium ion which acts as the carrier of the chain reactions is produced only from the isocyanide component, but not from the cyanide component. In other words, scheme 1 in Diagram I is not reversible.

In order to obtain further support for Diagram I, some relating reactions were examined. Triethyloxonium fluoroborate, $Et_3O^+BF_4^-$, was employed as the source of ethyl cation, which was subjected to the reaction with **6a**. The products were ethyl cyanide (**29**), N-ethylpivaloimidoyl cyanide (**30**), and N-ethylpivaloamide (**31**) in addition to the regular products formed in the $BF_3 \cdot OEt_2$ catalyzed reaction of **6a**. Ethyl cyanide is derived from the decomposition of the intermediate imidoyl cation (**32**), which is to be produced by the electrophilic addition of ethyl cation to **6a**. However, N-t-butylpropionimidoyl cyanide (**33**) which could be produced *via* the imidoyl cation **32**, was not formed. These results may be explained by assuming that **32** is readily decomposed into ethyl cyanide and t-butyl cation. t-Butyl cation thus produced would initiate the isomerization and dimerization of **6a**. Two products, **30** and **31**, are derived from N-ethylpivaloimidoyl cation (**34**) which is produced from t-butyl cyanide and ethyl cation.

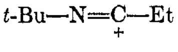
EtCN
29



$$t\text{-Bu—}\underset{\displaystyle CN}{\underset{|}{C}}\text{=N—Et}$$

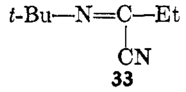
30

t-Bu—CONH—Et
31



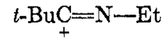
$$t\text{-Bu—N=}\underset{+}{C}\text{—Et}$$

32



$$t\text{-Bu—N=}\underset{\displaystyle CN}{\underset{|}{C}}\text{—Et}$$

33



$$t\text{-Bu}\underset{+}{C}\text{=N—Et}$$

34

Moreover, the reactions of **6a** with an imidoyl chloride and with an imidoyl cation complex (nitrilium salt) were investigated. Imidoyl chloride is a typical reagent of the Vilsmeier reaction, which is known to provide a typical imidoyl cation. The reaction of

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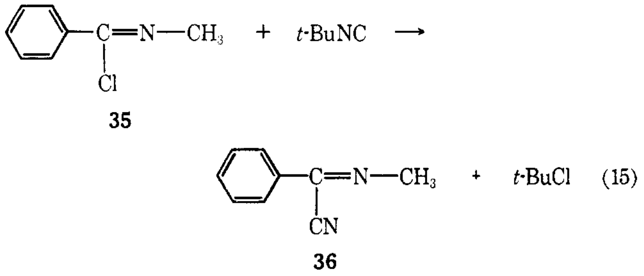
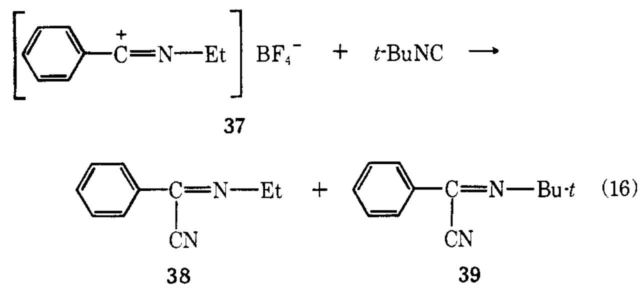
[6] N. J. Leonard and E. W. Nommensen, *J. Amer. Chem. Soc.*, **71**, 2808 (1949).

[7] J. J. Ritter and P. P. Minieri, *ibid.*, **70**, 4045 (1948).

6a with N-methylbenzimidoyl chloride (**35**) without any added catalyst produced N-methylbenzimidoyl cyanide (**36**) in a fairly high yield. The imidoyl cation is reasonably assumed as a key intermediate. N-Ethylbenzimidoyl fluoroborate (**37**) was employed as the second source of an imidoyl cation, which was prepared *in situ* according to Meerwein's method.[8] The reaction of **6a** and **37** gave two imidoyl cyanides, **38** and **39**. The formation of **39** is taken to indicate the existence of *t*-butyl cation. The ethyl-*t*-butyl exchange may occur in the imidoyl fluoroborate **37**. N-*t*-Butylbenzimidoyl hexachloroantimonate (**40**) was isolated and treated with **6a** to give similar results. However, the reaction of **6a** with N-*t*-butylacetoimidoyl hexachloroantimonate (**41**) brought about a different result, in which acetonitrile and an imidoyl cation (**42**) were produced. This reaction is explained by a nucleophilic replacement of **41** by **6a**.



(15)



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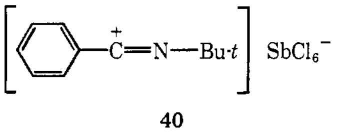

40

$$\underset{\mathbf{41}}{[CH_3\overset{+}{C}{=}N{-}Bu\text{-}t]SbCl_6^-} + t\text{-}BuNC \rightleftharpoons CH_3CN + \underset{\mathbf{42}}{[t\text{-}Bu{-}N{=}\overset{+}{C}{-}Bu\text{-}t]SbCl_6^-} \quad (17)$$

Experimental Section

Reactions of *t*-Butyl Isocyanide (6a) with $BF_3 \cdot OEt_2$.—Under nitrogen atmosphere at room temperature, 1.5 mmol of $BF_3 \cdot OEt_2$ in 1.5 ml of methylene chloride was added dropwise to 0.88 ml (10 mmol) of **6a** in 10 ml of methylene chloride. An exothermic reaction began immediately, and the reaction mixture turned red-brown, evolving gas of low boiling point. The gas was shown to be isobutylene (5% yield) by glpc and nmr spectrum analysis. The mixture was allowed to stand at room temperature for 1 day, and then was quenched with aqueous sodium bicarbonate. The methylene chloride layer was washed twice with 20 ml of water and then subjected to distillation. From the volatile fraction, *t*-butyl cyanide (**7a**) was obtained, in a yield of 49%, bp 105°.

Anal. Calcd for C_5H_9N: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.98; H, 11.04; N, 16.33.

From the second fraction [bp 100–120° (160 mm)], N-*t*-butylpivalimidoyl cyanide (**8a**) was obtained by means of preparative glpc, in a yield of 16%. The analytical data are shown in Table III. N-(N′-*t*-Butylpivalimidoyl)pivalimidoyl cyanide (**9a**) was isolated from the fraction of bp 100–150° (5 mm) by preparative glpc.

Anal. Calcd for $C_{15}H_{27}N_3$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.42; H, 10.89; N, 16.72.

The nmr spectrum of **9a** in $CDCl_3$ exhibits three sharp singlets at τ 8.53, 8.75, and 8.83 for *t*-Bu. The ir spectrum (neat) showed absorption at 2240 (C≡N), 1650 and 1620 cm^{-1} (C=N).

Hydrolysis of N-*t*-Butylpivalimidoyl Cyanide (8a).—A mixture of 0.5 g (3 mmol) of **8a** in 5 ml of methylene chloride and 1 ml of concentrated HCl was refluxed for 1 hr, and the mixture was added to excess aqueous sodium carbonate. The methylene chloride extracts were washed with water and distilled at atmospheric pressure to yield pivaloyl cyanide (**10a**) quantitatively, which was identified by comparison of the glpc retention time and infrared spectrum with the authentic sample prepared by the reaction of pivaloyl chloride with cuprous cyanide.

Hydrolysis of N-(N′-*t*-Butylpivalimidoyl)pivalimidoyl Cyanide (9a).—The reaction procedure was almost the same as described above. The main product was proved to be N-*t*-butylpivalamide (**11**) by comparison with the authentic sample.

Reaction of 3-Methylpentyl 3-Isocyanide (6b) by $BF_3 \cdot OEt_2$.—The procedure employed was virtually that of **6a**. The work-up of the reaction mixture as described above gave 3-methylpentyl 3-cyanide (**7b**) in a yield of 74% and dimer **8b** in a yield of 3%. The ir spectrum of **7b** had an absorption at 2250 cm^{-1} ($\nu_{C\equiv N}$).

Anal. Calcd for $C_7H_{13}N$: C, 75.62; H, 11.78; N, 12.60. Found: C, 75.62; H, 11.89; N, 12.78.

The characterization of **8b** is shown in Table III.

Reaction of 6a with Cyclohexyl Isocyanide.—To a solution of 0.88 ml of **6a** (10 mmol) and 1.2 ml of cyclohexyl isocyanide (10 mmol) in 10 ml of methylene chloride was added dropwise 1.5 mmol of $BF_3 \cdot OEt_2$ in 1.5 ml of methylene chloride with stirring at room temperature. After standing 1 day, the reaction system was treated with aqueous sodium bicarbonate. The methylene chloride layer was subjected to distillation. From the distillate, bp 50–150° (5 mm), N-cyclohexylpivalimidoyl cyanide (**12a**) and N-cyclohexylpivalamide (**13**) were isolated by preparative glpc in yields of 9 and 2%, respectively. Compound **13** was identified by comparison of its glpc retention time and ir with those of the authentic sample. From the residue, the low molecular weight cooligomer (average mol wt, 430) was obtained by silica gel column chromatography as the main product.

Reaction of 6a with 3-Methylpentyl 3-Isocyanide.—The reaction procedure was almost the same as the described above. A fraction collected by preparative glpc contained **15** and **16**. Nmr spectrum of the mixture revealed that the ratio of **15** to **16** was 1:2. The formation of **8a** and **8b** was indicated also by glpc.

Reaction of 6a with Phenyl Isocyanide.—In a similar way, the reaction of *t*-butyl isocyanide with phenyl isocyanide gave N-phenylpivalimidoyl cyanide (**12b**) (bp 90–95° (11 mm)) in a yield of 30%.

Reaction of 6a with Benzonitrile.—To a mixture of 0.88 ml (10 mmol) of **6a**, 1.02 ml (10 mmol) of benzonitrile, and 10 ml of methylene chloride, 1.5 mmol of $BF_3 \cdot OEt_2$ in 1.5 ml of methylene chloride was added dropwise at room temperature. After standing 1 day at the same temperature, the reaction system was quenched with aqueous sodium bicarbonate. The methylene chloride layer was subjected to distillation to give three products in addition to *t*-butyl cyanide (**7a**) and N-*t*-butylpivalimidoyl cyanide (**8a**) by glpc analysis. As a major product N-*t*-butylbenzimidoyl cyanide (**18c**) was obtained in a yield of 37% (bp 96–98° (11 mm); the product was identified by ir and nmr spectrum, and by its hydrolysis and hydrogenation products. Trace amounts of N-*t*-butylbenzamide and N-*t*-butyl-2-phenylglyoxylamide were detected, which were identified by the comparison of the glpc retention times and infrared spectrum with those of the respective authentic samples.

Hydrolysis of N-*t*-Butylbenzimidoyl Cyanide (18c).—The procedure was almost the same as that described for the hydrolysis of **8a**. Benzoyl cyanide was obtained quantitatively and was identified by the comparison of its glpc retention times and infrared spectrum with those of the authentic sample prepared by the reaction of benzoyl chloride with cuprous cyanide.

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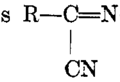
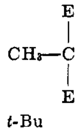
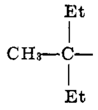
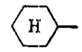
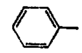
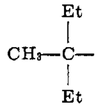
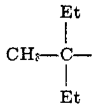
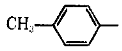
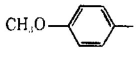
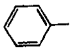
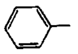
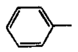
[8] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1940).

TABLE III

CHARACTERIZATIONS OF IMIDOYL CYANIDES


$R—\underset{\displaystyle CN}{\underset{|}{C}}=N—R'$

Compound	R	R′	Yield, %	Formula	Anal Calcd, % C	Anal Calcd, % H	Anal Calcd, % N	Anal Found % C	Anal Found % H	Anal Found % N	Ir spectrum, cm⁻¹ $\nu_{C\equiv N}$	Ir spectrum, cm⁻¹ $\nu_{C=N}$	Nmr absorption, τ
8a	*t*-Bu	*t*-Bu	49	$C_{10}H_{18}N_2$	72.24	10.91	16.85	72.00	11.13	16.55	2150 2250	1630	s 8.63 (9 H) s (8.82 (9 H)
8b	 $CH_3—\overset{\displaystyle Et}{\overset{\lvert}{\underset{\displaystyle Et}{\underset{\lvert}{C}}}}—$	 $CH_3—\overset{\displaystyle Et}{\overset{\lvert}{\underset{\displaystyle Et}{\underset{\lvert}{C}}}}—$	8	$C_{14}H_{26}N_2$	75.62	11.78	12.60	75.85	12.00	12.75	2160	1630	s 8.67 (3 H) s 8.94 (3 H)
12a	*t*-Bu		8	$C_{12}H_{20}N_2$	74.92	10.50	14.58	74.97	10.57	14.40	vw	1630	m 6.2–6.7 (1 H) m 8.0–9.0 (10 H) s 8.80 (9 H)
12b	*t*-Bu		30	$C_{12}H_{14}N_2$	77.38	7.58	15.04	77.24	7.87	14.96	2240	1630	m 2.5–3.2 (5 H) s (8.63 (9 H)
15	 $CH_3—\overset{\displaystyle Et}{\overset{\lvert}{\underset{\displaystyle Et}{\underset{\lvert}{C}}}}—$	*t*-Bu	12	$C_{12}H_{22}N_2$	74.17	11.41	14.42	74.34	11.51	14.53	vw	1630	m 8.1–8.5 (4 H) s 8.60 (9 H) s 8.93 (3 H) t 9.21 (6 H)
16	*t*-Bu	 $CH_3—\overset{\displaystyle Et}{\overset{\lvert}{\underset{\displaystyle Et}{\underset{\lvert}{C}}}}—$	11	$C_{12}H_{22}N_2$	74.17	11.41	14.42	74.71	11.27	14.41	2240	1635	q 8.36 (4 H) s 8.67 (3 H) s 8.80 (9 H) t 9.16 (6 H)
18d		*t*-Bu	40	$C_{13}H_{16}N_2$	77.96	8.05	13.99	77.97	7.98	13.76	2240	1610	d 2.16 (2 H) d 2.83 (2 H) s 7.59 (3 H) s 8.48 (9 H)
18e		*t*-Bu	37	$C_{13}H_{16}N_2O$	72.19	7.46	12.95	72.43	7.53	13.01	2270	1610	d 2.13 (2 H) d 3.13 (2 H) s 6.18 (3 H) s 8.50 (9 H)
30	*t*-Bu	Et	8	$C_8H_{14}N_2$	69.52	10.21	20.27	69.54	10.25	19.53	2240	1635	q 6.25 (2 H) t 8.73 (3 H) s 8.75 (9 H)
33	Et	*t*-Bu	6	$C_8H_{14}N_2$	69.62	10.21	20.27	69.51	10.33	19.78	2240	1648 1630	q 7.45 (2 H) s 8.59 (9 H) t 8.80 (3 H)
36		CH_3	46	$C_9H_8N_2$	74.98	5.59	19.43	74.19	5.61	19.06	2260	1615	m 2.0–2.8 (5 H) s 6.16 (3 H)
38		Et	29	$C_{10}N_{10}N_2$	75.92	6.37		76.60	6.42		2240	1610	m 1.8–2.7 (5 H) q 5.95 (2 H) t 8.57 (3 H)
39		*t*-Bu	37	$C_{12}H_{14}N_2$	77.38	7.58	15.04	77.56	7.54	15.20	2240	1610	m 2.0–2.8 (5 H) s 8.47 (9 H)

Hydrogenation of N-*t*-Butylbenzimidoyl Cyanide (18c) with LiAlH$_4$.—To a stirred solution of 1 g (26 mmol) of LiAlH$_4$ in 20 ml of ethyl ether, 2.1 g (11 mmol) of **18c** in 15 ml of ethyl ether was added dropwise at −78° during a 15-min period. Stirring was then continued for an additional 24 hr at the reflux temperature. The reaction mixture was hydrolyzed and the ethyl ether layer was distilled *in vacuo* to give 1.5 g of N′-*t*-butyl-1-phenylethylenediamine (**43**), bp 92–94° (12 mm).

Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 74.74; H, 10.62; N, 14.62.

The nmr spectrum of **43** in $CDCl_3$ showed three multiplets at τ 2.74 (5 H, phenyl), 6.32 (1 H, CH), and 7.30 (2 H, CH_2), singlet at 8.60 (3 H, NH, NH_2), and singlet at 9.00 (9 H, *t*-Bu). The singlet at τ 8.60 disappeared in the D_2O treatment.

Reaction of *t*-Butyl Isocyanide with Other Nitriles.—The reaction procedure was almost the same as that described above. The main products were N-*t*-butylimidoyl cyanides, which are summarized in Table II.

Reaction of 6a with Triethyloxonium Fluoroborate.—A solution of 3.3 g (40 mmol) of **6a** in 15 ml of methylene chloride was added to 3.8 g (20 mmol) of triethyloxonium fluoroborate in 20 ml of methylene chloride with stirring at 0° over 40 min. After standing 1 hr, the mixture was warmed to room temperature and stirred for an additional 18 hr, and then poured into aqueous sodium carbonate. The methylene chloride layer was washed twice with 20 ml of water and distilled to give 1.44 mmol (8%) of propionitrile (**29**) and 1.2 mmol (6%) of N-ethylpivalimidoyl Cyanide (**30**) in addition to 16.5 mmol (41%) of **7a** and 2.9 mmol (15%) of **8a**. From the residue of distillation, N-ethylpivalamide (**31**) was isolated in 3% yield, but the isomeric amide N-*t*-butylpropioamide was not detected.

Reaction of *t*-Alkyl Isocyanide with N-Methylbenzimidoyl Chloride (35).—To a solution of 1.1 g (7 mmol) of **35** in 10 ml of methylene chloride, 1.66 g (20 mmol) of **6a** was added dropwise at room temperature. After standing for 1 day at the same temperature, the reaction mixture was poured into aqueous sodium bicarbonate. The methylene chloride layer was distilled to give N-methylbenzimidoyl cyanide (**36**) in 47% yield.

Reaction of 6a with N-Ethylbenzimidoyl Fluoroborate (37).—Compound **37** was prepared *in situ* by Meerwein's method; *i.e.*, 3.8 g (20 mmol) of triethyloxonium fluoroborate was treated with 1.0 g (10 mol) of benzonitrile in 20 ml of methylene chloride for 2 days at room temperature. To this solution, 0.83 g (10 mmol) of **6a** in 10 ml of methylene chloride was added dropwise over 40 min. After standing for 2 hr, the reaction mixture was poured into aqueous sodium bicarbonate, and the methylene chloride layer was distilled to give N-ethylbenzimidoyl cyanide (**38**) (29% yield) along with N-*t*-butylbenzimidoyl cyanide (**39**) (19% yield).

Reaction of 6a with N-*t*-Butylbenzimidoyl Hexachloroantimonate (40).—A mixture of 5.0 g (10 mmol) of **40** in 20 ml of methylene chloride and 0.83 g (10 mmol) of **6a** was kept at room temperature to produce **39** in 8% yield.

Registry No.—**6a**, 7188-38-7; **7a**, 630-18-2; **7b**, 21864-76-6; **8a**, 21864-77-7; **8b**, 21864-78-8; **9a**, 21864-79-9; **12a**, 21864-80-2; **12b**, 21864-81-3; **15**, 21864-82-4; **16**, 21864-83-5; **18d**, 21864-84-6; **18e**, 21864-85-7; **30**, 21864-86-8; **33**, 21864-87-9; **36**, 21864-88-0; **38**, 21864-89-1; **39**, 21864-90-4; **43**, 21876-36-8; boron trifluoride diethyl ether, 109-63-7.

Photodimeric Cage Compounds. II. The Structure of the Photodimer of 2,6-Diethyl-4-pyrone[1]

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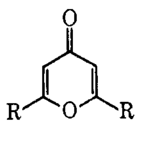
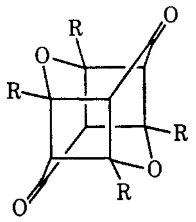
Spectroscopic and degradative studies show that the photodimer of 2,6-diethyl-4-pyrone has the head-to-tail cage structure **4**, analogous to that of the photodimer of 2,6-dimethyl-4-pyrone.

The photodimer[3] of 2,6-dimethyl-4-pyrone (**1**) has been shown to have the cage structure **2**.[1] This photodimerization is unusual in that it proceeds with regiospecificity[4] and stereospecificity to give a single *cis-syn-cis* head-to-tail dimer.[5] Irradiation of 2,6-diethyl-4-pyrone (**3**) also leads to a single photodimer, which has been assigned the cage structure **4** on the basis of the similarity of its properties to those of the dimer **2**.[6] We now report on an investigation of the chemistry of the photodimer of **3**, which fully establishes its structure as **4**.



1, R = CH_3
3, R = C_2H_5



2, R = CH_3
4, R = C_2H_5

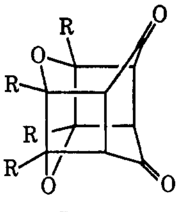
The monomer **3** was prepared from acetonedicarboxylic acid *via* treatment with propionic anhydride in the presence of sulfuric acid in an adaptation of the procedure of Deshapande.[7] Irradiation of **3** as the neat liquid, or better in solution in ethanol or benzene, led to the deposition of a solid dimer. In the latter solvent a 46% conversion to crystalline dimer, mp 273–275° dec, was realized after irradiation with a 450-W Hanovia medium-pressure arc lamp for 10 days; since the reaction solution contained *ca.* 50% of unconsumed monomer, the yield was *ca.* 90%. Comparison of the spectra of this dimer with those of the dimer of 2,6-dimethyl-4-pyrone (Table I) revealed a close similarity. The nmr spectrum of **2**, which has not been reported previously, and that of **4** are clearly in accord with the structural assignments. The unusually low-field position of the methine proton signals may be interpreted as due to deshielding by the neighboring carbonyl groups, in whose planes these protons are rigidly held. It must be emphasized, however, that these nmr spectra do not in themselves distinguish between the head-to-tail cage structures **2** and **4** and the corresponding head-to-head cage structures **5** and **6**, respectively.

TABLE I

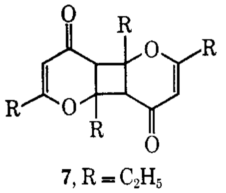
SPECTRA OF THE PHOTODIMERS OF 2,6-DIMETHYL- AND 2,6-DIETHYL-4-PYRONE

Spectrum	2,6-Dimethyl-4-pyrone photodimer (**2**)	2,6-Diethyl-4-pyrone photodimer (**4**)
Infrared, $\lambda_{max}^{CHCl_3}$, μ	5.88, 6.90, 7.24	5.80,[a] 5.89, 6.90, 7.24
Ultraviolet, λ_{max}^{EtOH}, mμ	233 (ε 6600)[b]	236 (ε 6700)
Nuclear magnetic resonance, δ^{CDCl_3}, ppm	1.50 (s, 12 H) 3.18 (s, 4 H)	0.90 (t, *J* 7 Hz, 12 H) 1.72 (q, *J* 7 Hz, 8 H) 3.16 (s, 4 H)

[a] Shoulder. [b] Molecular extinction coefficient recorded for solution in acetonitrile; position of maximum unchanged.



5, R = CH_3
6, R = C_2H_5



7, R = C_2H_5
8, R = CH_3

The retention of the skeletal integrity of each of the monomer units in the dimer of **3** was established as in the case of the dimer of **1**[1] by the observation that treatment with aqueous methanolic hydrogen chloride returned the monomer in *ca.* 70% yield. Under milder acidic conditions it was possible to halt the reaction after the cleavage of a single cyclobutane ring and to isolate the *seco*-dimer **7**; this product was also obtained when the cage dimer was treated with ethyl-

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(1) Paper I: P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963).

(2) (a) Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Ontario, Canada; Alfred P. Sloan Foundation Fellow, 1957–1960; Hoffmann La Roche Fellow, 1961–1963; (b) Eastman Kodak Co. Fellow, Harvard University, 1959–1960; (c) Commonwealth Scholar, University of Toronto, 1963–1966.

(3) E. Paternò, *Gazz. Chim. Ital.*, **44**, I, 151 (1914); M. Giua and M. Civera, *ibid.*, **81**, 875 (1951).

(4) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

(5) *Cf.*, for example, P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2344 (1962); H. Ziffer, N. E. Sharpless, and R. O. Kan, *Tetrahedron*, **22**, 3011 (1966); P. Yates, S. N. Eğe, G. Büchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967); S. N. Eğe and P. Yates, *ibid.*, **45**, 2933 (1967); E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3482 (1967); O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Rec. Chem. Progr.*, **28**, 167 (1967).

(6) P. Yates and E. S. Hand, *Tetrahedron Lett.*, 669 (1961); E. S. Hand, Ph.D. Thesis, Radcliffe College, 1961.

(7) S. S. Deshapande, *J. Indian Chem. Soc.*, **9**, 303 (1932).