[3.2.1.0^{2,4}]octan-8-ol (V) present. Glpc on the UCON LB 550X capillary column at 115° showed that the minor component was present as 14 ± 3% of the mixture.

endo-anti Alcohol V in the presence of p-Nitrobenzoic Acid. endo-anti-Tricyclo[3.2.1.0^{2,4}]octan-8-ol (53.4 mg, 0.43 mmole) and 73.8 mg (0.44 mmole) of p-nitrobenzoic acid were dissolved in 42 ml of 70% aqueous dioxane in a 50-ml flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated at 100° for 16 hr. Extraction with pentane, washing with 10% aqueous Na$_2$CO$_3$ solution, drying, and removal of solvent (see above work-up) gave 48 mg (90%) of a white solid. Glpc on the

UCON LB 550X capillary column at 115° showed that the product was a 1:4 mixture of endo-tricyclo[3.3.0.0^{4,6}]octan-2-ol and endo-anti-tricyclo[3.2.1.0^{2,4}]octan-8-ol. endo-anti alcohol V is only slowly rearranged under the product study conditions given above.

On the Mechanism of the Free-Radical Reactions of Cyanogen and Cyanogen Chloride with Hydrocarbon Substrates[1]

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Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. Received November 4, 1968

Abstract: Both the free-radical reactions of cyanogen chloride and cyanogen with hydrocarbon substrates proceed by chain mechanisms involving intermediate imidyl radicals. In the reaction of cyanogen with 2,3-dimethylbutane the imidyl radical was found to be the chain-carrying species while in the reactions of cyanogen chloride with a variety of hydrocarbons, the imidyl intermediate undergoes a β-scission reaction producing the alkyl cyanide plus a chlorine atom which then carries the chain. The mechanism of the cyanation reaction of cyanogen chloride has been shown to proceed through a chain sequence of reactions in which each step was demonstrated to be reversible. The high selectivity observed in these cyanations was found to be due to the reversible reaction of the alkyl radicals formed with the hydrogen chloride produced in the reactions.

The photochemical reaction between cyanogen chloride and certain hydrocarbons has recently been reported by Müller and Huber.[3] Moderate yields of cyclohexyl cyanide (10%) were obtained from the reaction between cyanogen chloride and cyclohexane, while in the presence of acetyl chloride[3a] or free chlorine[3c] the yield was much improved.

$$C_6H_{12} + ClCN \xrightarrow{h\nu} C_6H_{11}CN + HCl \qquad (1)$$

The authors proposed a radical chain mechanism in which the chain-propagating step was the abstraction of hydrogen by chlorine atoms. The radicals so formed then underwent a radical displacement upon the carbon of cyanogen chloride, a rare if not unique reaction[4] (Scheme I), to give the alkyl cyanide.

Scheme I

$$Cl\cdot + RH \longrightarrow HCl + R\cdot \qquad (2)$$

$$R\cdot + ClCN \longrightarrow RCN + Cl\cdot \qquad (3)$$
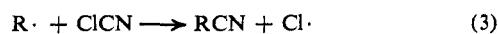
Although there are a few reports in the patent literature of the reactions of cyanogen chloride with alkanes[5] and alkenes[6-8] these involved very drastic temperatures and were very unselective reactions.

There are also reports of the reaction of cyanogen chloride with ethyl vinyl ether to give 2-ethoxy-3-chloroproprionitrile[9] and with saturated alkanes to give alkyl cyanides[10] both of which required the presence of peroxy compounds as radical initiators.

Because of the novelty of the chain-transfer reaction (eq 3) and because of the potential synthetic utility of a free-radical cyanation process, a detailed investigation of the mechanism of the reaction was undertaken.

Results and Discussion

Peroxide-Initiated Cyanation. The chain nature of the cyanation was established by initiation of the reaction with benzoyl peroxide. By treating cyanogen chloride (0.8 M) with various hydrocarbons in the presence of benzoyl peroxide (3 mole %), and determining the yield of alkyl cyanides, an approximate chain length of 6–15 units, depending on the substrate, was found. The efficiency for benzoyl peroxide initiation was taken, in these calculations,[11] to be 0.5. When 2,3-dimethylbutane was the substrate, minor amounts of alkyl chlorides were also formed. At higher initiator concentrations the ratio of alkyl

(1) Presented in part at the Division of Organic Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

(2) University of Alberta, Killam Memorial Post-Doctoral Fellow, 1967–1969.

(3) (a) E. Müller and H. Huber, Chem. Ber., 96, 670 (1963); (b) ibid., 96, 2319 (1963); (c) German Patent 1,129,157 (1962); Chem. Abstr., 57, 13627g (1962).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 32.

(5) J. K. Dixon, U. S. Patents 2,553,404 (1951), 2,553,406 (1951); Chem. Abstr., 45, 9081 (1951).

(6) W. L. Kohlhase and T. F. Martens, U. S. Patents 2,848,476 (1958), 2,848,477 (1958); Chem. Abstr., 53, 2093i (1959).

(7) J. K. Dixon, U. S. Patent 2,745,864 (1956); Chem. Abstr., 51, 2019b (1957).

(8) H. Brendlein, U. S. Patent 2,833,808 (1958); Chem. Abstr., 52, 14659c (1958).

(9) E. I. Vasil'eva, B. I. Keda, and R. Kh. Freidlina, Dokl. Akad. Nauk, SSSR, 154, 129 (1964).

(10) R. Graf, German Patent 848,947 (1952); Chem. Abstr., 47, 5425b (1953).
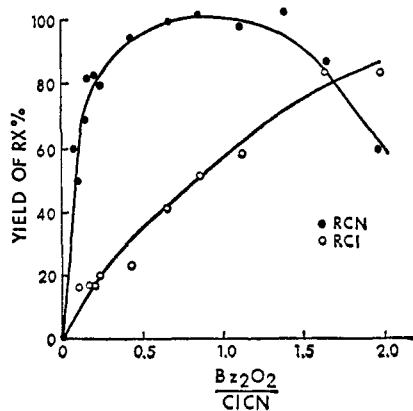
(11) Reference 4, pp 73–80.

Figure 1. The reaction of cyanogen chloride with 2,3-dimethylbutane at 98° in the presence of benzoyl peroxide.
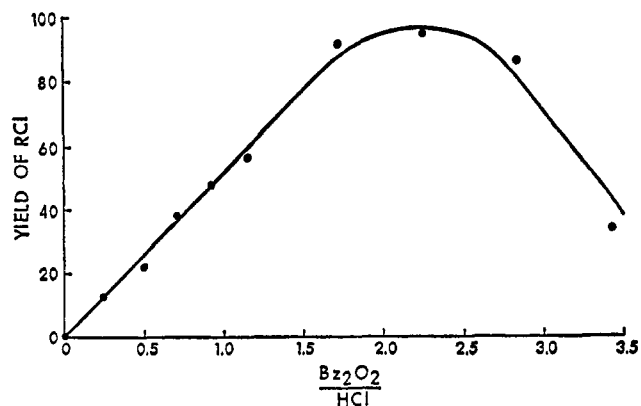

Figure 2. The reaction of hydrogen chloride with cyclohexane at 98° in the presence of benzoyl peroxide.

cyanide to alkyl chloride became smaller (see Figure 1). Similar behavior was observed with cyclohexane.

At 64 mole % benzoyl peroxide a 90% yield, based on cyanogen chloride, of alkyl cyanide was produced, while 35% of the available chlorine appeared as the alkyl chloride.

The possibility that the alkyl chloride was produced by a reaction between hydrogen chloride, a by-product of the alkyl cyanide forming reaction (eq 1), and benzoyl peroxide was considered for the following reasons. First, the ratio of alkyl cyanide to alkyl chloride varied with different peroxide concentrations. Second, only traces of alkyl chloride were produced upon photo-initiation of the reaction. Furthermore, the fact that the yield of alkyl cyanide and alkyl chloride, taken together, exceeded 100% of the initial quantity of cyanogen chloride implied that an oxidation reaction had occurred.

The reaction between hydrogen chloride (0.24 M) and cyclohexane (2.5 M), in the presence of varying quantities of benzoyl peroxide, was therefore carried out in acetonitrile at 98°. The yield of cyclohexyl chloride was determined by glpc analysis. The results of a series of reactions in which the mole ratio of benzoyl peroxide to hydrogen chloride ranged from 0 to 3.42 are seen in Figure 2. The oxidation of alkanes to alkyl chlorides by hydrogen chloride and benzoyl peroxide was found to be a nearly quantitative reaction under the conditions used for the reactions of cyanogen chloride with these substrates. The production of alkyl chloride in the cyanation reaction can undoubtedly be attributed to this oxidation reaction, the details of the mechanism of which are presently under investigation and will be reported elsewhere.

Consideration of Possible Mechanisms. The mechanism proposed by Müller for the cyanation of hydrocarbons by cyanogen chloride involves the chlorine atom as the hydrogen atom abstracting species (Scheme I). We would therefore expect, for substrates containing hydrogen atoms in different environments, to see a distribution of isomeric cyanides reflecting the hydrogen atom selectivity of chlorine atoms. However, the photolysis of a 2,3-dimethylbutane solution of cyanogen chloride (0.6 M) in quartz ampoules with the light from a 450-W high-pressure mercury arc, gave the tertiary cyanide (α,α,β-trimethylbutyronitrile) in a yield of 30%, while no primary cyanide (β,γ-dimethylvaleronitrile)

could be detected. If chlorine is the abstracting species, as in the mechanism of Müller and Huber, we would expect[12] the respective ratio to be 6:5. The apparent incompatibility of the Müller mechanism with the high selectivity found in the cyanation reaction prompted us to seek other mechanistic pathways to explain the observed product distribution.

One possible chain mechanism leading to alkyl cyanide involves hydrogen abstraction by a cyanide (CN·) radical. In this proposed sequence the hydrogen cyanide formed reacts with cyanogen chloride in an ionic reaction to give hydrogen chloride and cyanogen. Subsequent displacement of a cyanide radical from cyanogen by an alkyl radical could then lead to the alkyl cyanide (Scheme II). This mechanism is

Scheme II

$$RH + CN· \longrightarrow R· + HCN$$

$$HCN + ClCN \longrightarrow HCl + NC-CN$$

$$R· + (CN)_2 \longrightarrow RCN + ·CN$$
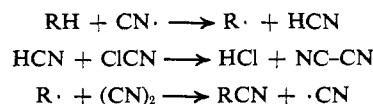
analogous to that involved in the bromination of hydrocarbons by N-bromosuccinimide[13] or their chlorination by N-chloramines.[14] This proposal requires that the cyanide radical have a high degree of selectivity, and that there be a favorable mechanistic path for the reaction between hydrogen cyanide and cyanogen chloride in solution. The latter reaction has been observed at elevated temperatures in the vapor phase[15] but no information is available on its ionic counterpart in solution.

Reaction between Cyanogen and 2,3-Dimethylbutane. The proposed radical displacement on cyanogen was investigated by studying the reaction of 2,3-dimethylbutane and cyanogen. Catalytic amounts of benzoyl peroxide promoted the radical chain reaction of cyanogen with the hydrocarbon substrate, but instead of the anticipated tertiary cyanide, a 1:1 adduct of the hydrocarbon and cyanogen was obtained in about 20% yield as the only observed product. The structure of the product was shown to be the iminocyanide (I), and its identity was established from its ir, nmr, and mass spectra, microanalysis, and by its conversion to the
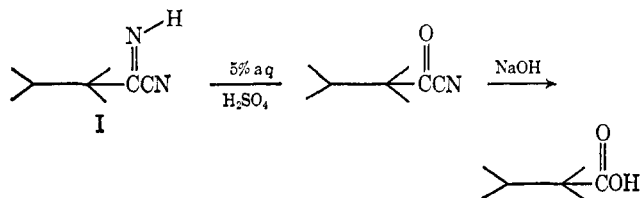
(12) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987, 4997 (1958).
(13) C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963), and references cited therein.
(14) D. D. Tanner and M. W. Mosher, *Can. J. Chem.*, **47**, 715 (1969).
(15) B. S. Lacey, H. A. Bond, and W. S. Hinegardner, U. S. Patent 2,399,361 (1946).

known α,α,β-trimethylbutyric acid by the following sequence of reactions.

Variation of the amount of initiator and glpc analysis gave an optimum yield of I of over 70%. The chain length was determined using catalytic amounts of initiator, giving an estimated chain length of approximately 5.

A reasonable chain mechanism can be proposed for the formation of the adduct which involves an imidyl radical as the chain-carrying species (Scheme III).

Scheme III
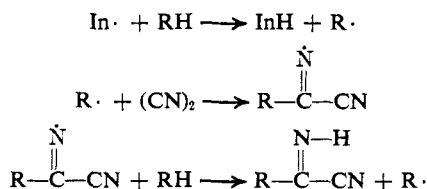
Since the tertiary adduct was the only product of the reaction of cyanogen with 2,3-dimethylbutane, no alkyl cyanide being formed, Scheme II cannot represent the mechanism of the reaction of cyanogen chloride with this substrate. The high selectivity observed in the formation of the adduct and in the cyanation reactions of cyanogen chloride suggested a similar intermediate in both reactions, a highly selective imidyl radical. This reaction sequence for the cyanation reactions of cyanogen chloride is seen in Scheme IV.
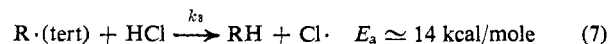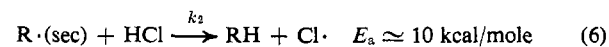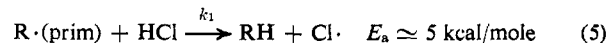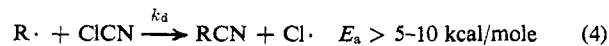
Scheme IV
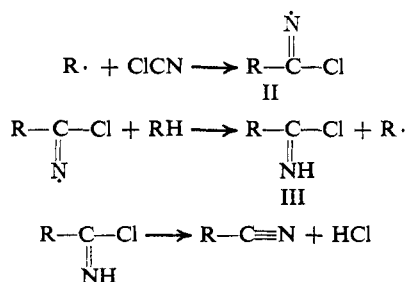
In this case the product of hydrogen abstraction by the imidyl radical II is the imino chloride III, but, since these are known to be thermally unstable[16] under the conditions of the reaction, it breaks down to give the observed products, alkyl cyanide and hydrogen chloride.

Reaction of Alkyl Radicals with Hydrogen Chloride. Empirically, the photochemical cyanation reaction seems to be a short-chain process, being characterized by low yields (10–30%) and long irradiation times (12–24 hr). The benzoyl peroxide initiated reactions described above also lead to this conclusion, which implies that at least one step in the chain must proceed with some difficulty. If the assumption is made that the formation of the imidyl radical is a high-energy
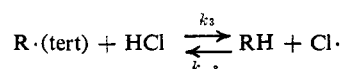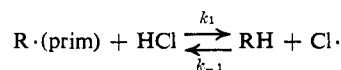
process ($E_a > 5$–10 kcal/mole), then an alternative explanation for the selectivity shown by the reagent may be offered. Since hydrogen chloride was produced in the reaction, a competitive reaction of the hydrocarbon radical between hydrogen chlorine and cyanogen chloride might be envisioned. A precedent for this suggestion is the finding[17] that γ irradiation of solutions of deuterium chloride in cyclohexane leads to incorporation of deuterium into the cyclohexane; the intermediacy of cyclohexyl radicals is indicated.

$$R\cdot + ClCN \xrightarrow{k_d} RCN + Cl\cdot \quad E_a > 5\text{–}10 \text{ kcal/mole} \quad (4)$$

$$R\cdot(\text{prim}) + HCl \xrightarrow{k_1} RH + Cl\cdot \quad E_a \simeq 5 \text{ kcal/mole} \quad (5)$$

$$R\cdot(\text{sec}) + HCl \xrightarrow{k_2} RH + Cl\cdot \quad E_a \simeq 10 \text{ kcal/mole} \quad (6)$$

$$R\cdot(\text{tert}) + HCl \xrightarrow{k_3} RH + Cl\cdot \quad E_a \simeq 14 \text{ kcal/mole} \quad (7)$$

The activation energies for the reactions of primary ($R\cdot(\text{prim})$), secondary ($R\cdot(\text{sec})$), and tertiary ($R\cdot(\text{tert})$) hydrocarbon radicals with hydrogen chloride were estimated by calculating the enthalpies of the reactions using known bond energies,[18] and adding to these values the known activation energies for abstraction of differing hydrogens by atomic chlorine.[19]

The calculated energies of activation suggest that the reaction of an alkyl radical with hydrogen chloride would be a selective process, and that the rate (k_1) of the reaction of a primary radical would be much greater than k_3, the rate of reaction of a tertiary radical. The argument can be illustrated for the case of the reaction of 2,3-dimethylbutane, where both primary and tertiary radicals can be formed by hydrogen abstraction. From

$$R\cdot(\text{prim}) + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RH + Cl\cdot$$

$$R\cdot(\text{tert}) + HCl \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RH + Cl\cdot$$

the previously calculated activation energies $k_1 \gg k_3$ and since the rate of abstraction of a tertiary hydrogen atom by atomic chlorine (k_{-3}) is greater than the rate (k_{-1}) of abstraction of a primary hydrogen atom,[20] the resulting equilibrium expression can be derived.

$$R\cdot(\text{prim}) \rightleftharpoons R\cdot(\text{tert})$$

Thus primary radicals can be reversibly converted to tertiary radicals and the resulting equilibrium constant would be much greater than unity. Similar results can be derived for the reactions of n-butane where primary and secondary radicals are involved.

$$R\cdot(\text{prim}) \rightleftharpoons R\cdot(\text{sec}) \quad K_{eq} \gg 1$$
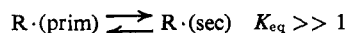
If the reaction of the radicals with hydrogen chloride occurred as fast as, or faster than, the reaction with cyanogen chloride, then the product distribution would show a higher selectivity than would be expected from the selectivity of the hydrogen-abstracting species.

(16) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1965, pp 169–170.

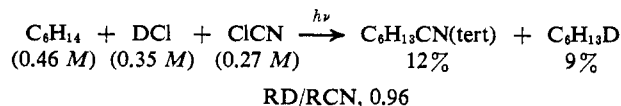(17) J. W. Fletcher and G. R. Freeman, *Can. J. Chem.*, **44**, 2645 (1966).

(18) Values for the C–H bond energies were taken from J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). The value 103.2 kcal/mole for D(H–Cl) was taken from ref 4, p 48.

(19) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, **1**, 11 (1965).

(20) J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959).
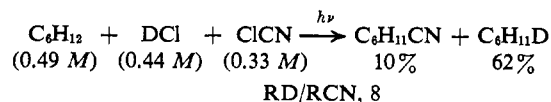
One would therefore obtain mainly tertiary product $k_1 > k_d$, i.e., $E_a(4) > E_a(5)$.

To test whether the exchange reaction was occurring, and to obtain an estimate of its importance relative to the cyanation reaction (eq 4), the photolysis of cyanogen chloride with alkanes was studied in the presence of deuterium chloride. When cyanogen chloride (0.27 M) reacted with a mixture of 2,3-dimethylbutane (0.46 M) and deuterium chloride (0.35 M) in acetonitrile, it was found that, when 12% of the cyanogen chloride had reacted to form the tertiary cyanide, 9% of the total deuterium was incorporated into the unreacted hydrocarbon.

$$C_6H_{14} + DCl + ClCN \xrightarrow{h\nu} C_6H_{13}CN(tert) + C_6H_{13}D$$
$$(0.46\ M)\ (0.35\ M)\ (0.27\ M) \qquad\quad 12\% \qquad\quad 9\%$$
RD/RCN, 0.96

From the ratio of the products formed, a lower limit could be estimated for the ratio of the number of exchanges to the number of displacements on cyanogen chloride (RD/RCN). This ratio was found to be approximately unity.
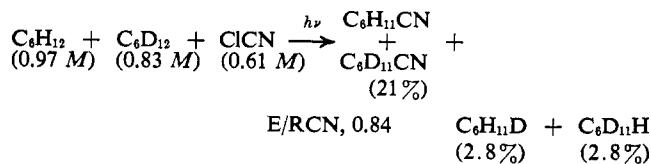
When the reaction was repeated using cyanogen chloride (0.33 M), deuterium chloride (0.44 M), and cyclohexane (0.49 M) as substrate, the photolysis in acetonitrile resulted in the incorporation of 62% of the available deuterium into the unreacted cyclohexane, while the conversion of cyanogen chloride to cyclohexyl cyanide was 10%. The lower limit for the ratio of

$$C_6H_{12} + DCl + ClCN \xrightarrow{h\nu} C_6H_{11}CN + C_6H_{11}D$$
$$(0.49\ M)\ (0.44\ M)\ (0.33\ M) \qquad 10\% \qquad 62\%$$
RD/RCN, 8

exchange to displacement was calculated to be 8:1.

At these high concentrations of deuterium chloride, exchange was thus shown to be important. Presumably the primary radicals, if formed in either the reaction of the hydrocarbon with cyanogen chloride or during the reversible reaction with deuterium chloride by chlorine atom abstraction, were the predominant ones undergoing the reaction with deuterium chloride.

The photoinitiated cyanation of a mixture of cyclohexane and perdeuteriocyclohexane with cyanogen chloride showed that the secondary cyclohexyl radicals give an appreciable exchange reaction at low conversions of cyanogen chloride (21%) to alkyl

$$C_6H_{12} + C_6D_{12} + ClCN \xrightarrow{h\nu} \begin{array}{c} C_6H_{11}CN \\ + \\ C_6D_{11}CN \end{array} +$$
$$(0.97\ M)\ (0.83\ M)\ (0.61\ M) \qquad\qquad (21\%)$$

$$E/RCN, 0.84 \qquad\quad C_6H_{11}D + C_6D_{11}H$$
$$(2.8\%) \qquad (2.8\%)$$

cyanides. Since both deuterium chloride and hydrogen chloride were produced in approximately equal amounts during the photolysis, a lower limit for E/RCN (where E = total number of exchanges = $R_DH + R_HD$) was calculated as 0.84.

It was apparent from the above experiments that the exchange reaction takes place with both primary and secondary radicals. The results indicate that its importance is dependent on the concentration of hydrogen chloride (i.e., the percentage reaction) and therefore the selectivity of the cyanation must be dependent on the extent of the reaction.

The photoinitiated reaction of a high concentration of cyanogen chloride in butane was studied at low conversions. This situation favors the reaction of an alkyl radical with cyanogen chloride rather than with hydrogen chloride. At differing conversions (i.e., various concentrations of hydrogen chloride) it was found, as predicted, that the selectivity was indeed a function of the percentage reaction (see Table I).

Table I. A Comparison of the Primary:Secondary Selectivity (per H) with Percentage Reaction in the Photocyanation of Butane
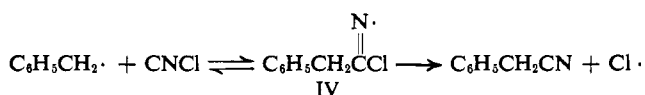
$$\text{\raise2pt\hbox{$\diagdown\!\diagup\!\diagdown$}} + CNCl(3.3\ M) \xrightarrow{h\nu}$$

$$\diagdown\!\diagup\!\diagdown\!\!-CN + \diagdown\!\!\underset{CN}{\diagup}\!\!\diagdown + HCl$$

% reaction	Prim/sec
5.2	1/168
0.91	1/24
0.16	1/6
(0.00)	(1/2)[a]

[a] Extrapolated value. The value 1/2 was obtained by fitting the experimentally obtained results to a quadratic equation.

If one extrapolated the results to 0% reaction (when there is no hydrogen chloride present) the selectivity observed was seen to be close to that predicted for the abstraction reactions reported for atomic chlorine.[12]

Reaction of Cyanogen Chloride with Toluene. Both the photoinitiated and the benzoyl peroxide initiated reactions of cyanogen chloride with toluene gave only low yields of the desired benzyl cyanide. This result could not be explained by the lack of abstraction of a benzylic hydrogen regardless of the abstracting species, since abstraction from toluene should be energetically favored over the abstraction of an alkyl hydrogen. The proposed high activation energy for alkyl radical addition to the C≡N bond of cyanogen chloride to give II would explain the difficulty of this addition by the more stable benzyl radical. Furthermore, if addition of the benzyl radical to cyanogen chloride did occur to form the intermediate imidyl radical IV, β scission of the intermediate to give cyanogen chloride and a stable benzyl radical (i.e., reversal of the process) might well be favored over the elimination of a chlorine atom. The enthalpy of the reaction was estimated[18]
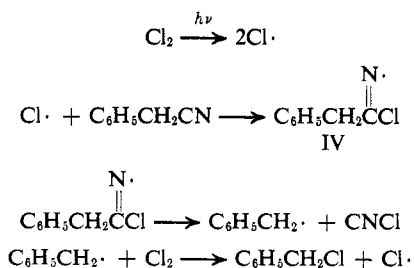
$$C_6H_5CH_2\cdot + CNCl \rightleftharpoons C_6H_5CH_2\overset{\overset{\displaystyle N\cdot}{\|}}{C}Cl \longrightarrow C_6H_5CH_2CN + Cl\cdot$$
$$IV$$

to be very close to zero.[21,22] The intermediacy of the imidyl radical IV and the reversibility of its formation were verified by using an independent method for its formation. When an acetonitrile solution of benzyl cyanide and molecular chlorine was photolyzed with incandescent light, small amounts of benzyl chloride and cyanogen chloride were obtained (see Scheme V). Although the reaction of chlorine atoms with benzyl cyanide to produce IV would not be a selective process,

(21) $D(PhCH_2-CN)$ was estimated to be close to 85 kcal/mole, using the observation that for a wide range of substituents (X) $D(CH_3-X) - D(PhCH_2-X) = 17 \pm 2$ kcal. $D(CH_3-CN)$ is given as 103 ± 2 kcal/mole.[18]
(22) G. Glocke, J. Phys. Chem., 63, 828 (1959), gives $D(Cl-CN)$ as 89 kcal/mole.

Scheme V

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$

$$Cl\cdot + C_6H_5CH_2CN \longrightarrow C_6H_5CH_2\overset{\overset{\displaystyle N\cdot}{\|}}{C}Cl$$
$$IV$$

$$C_6H_5CH_2\overset{\overset{\displaystyle N\cdot}{\|}}{C}Cl \longrightarrow C_6H_5CH_2\cdot + CNCl$$
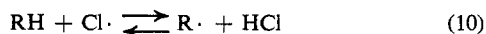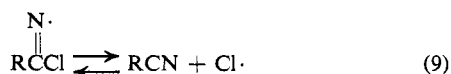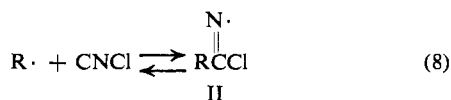
$$C_6H_5CH_2\cdot + Cl_2 \longrightarrow C_6H_5CH_2Cl + Cl\cdot$$

since ring chlorination and hydrogen abstraction are both more probable, the chlorine atom addition to the cyanide does proceed to a sufficient extent to allow the characterization of the products of β scission.

Mechanistic Conclusions. The mechanistic path which is consistent with our experimental observations is seen in Scheme VI. It will be observed that 8 and 9

Scheme VI

$$R\cdot + CNCl \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} R\overset{\overset{\displaystyle N\cdot}{\|}}{C}Cl \qquad (8)$$
$$II$$

$$R\overset{\overset{\displaystyle N\cdot}{\|}}{C}Cl \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} RCN + Cl\cdot \qquad (9)$$

$$RH + Cl\cdot \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} R\cdot + HCl \qquad (10)$$

in this scheme take the place of eq 3 in Scheme I, which means that the radical displacement upon carbon, implied in the latter scheme, can be better represented as an addition/β scission sequence. It therefore appears that a radical displacement of carbon in the reactions of nitriles remains to be established, and that the reported displacement of the trifluoromethyl radical from trifluoroacetonitrile[23] may well fall into the category of an addition/β scission reaction.

The reversible formation of the imidyl radical II, produced either by alkyl radical addition to cyanogen chloride (eq 8) or by the addition of a chlorine atom to the C≡N bond of the alkyl cyanide (eq 9), is proposed by analogy to the imidyl radical formed in the reaction of alkyl radicals with cyanogen as shown in Scheme III. That the chain-carrying species in the cyanation reactions of cyanogen chloride is atomic chlorine was established from the extrapolated values for the selectivity obtained in the low-conversion cyanation of n-butane, while the reversibility of the hydrogen abstraction was demonstrated by the deuterium-exchange experiments. The apparent high selectivity exhibited during the radical cyanation reaction is controlled by the selective reversibility of the primarily formed radicals with hydrogen chloride.

Synthesis of Nitriles. The peroxide-initiated formation of alkyl cyanides with cyanogen chloride has been reported in the patent literature.[5,10] In order to establish the synthetic utility of this reaction in the context of our mechanistic studies, a representative number of alkyl cyanides were prepared by the benzoyl peroxide initiated reaction of cyanogen chloride in solvent acetonitrile or using the hydrocarbon as solvent. An important synthetic feature of the mechanism is the result of the high selectivity observed; secondary, and particularly tertiary cyanides are formed pref-

erentially. These are the more difficult cyanides to prepare by other methods.[24] In the case of the cyanation of neopentane and n-butane, acetonitrile was used as a solvent in order to decrease the vapor pressure of the hydrocarbons. However, we consistently noticed lower yields in the presence of any cosolvent. At about 15–20 mole % benzoyl peroxide the alkyl cyanide was the major product and could be isolated by preparative glpc. The products and yields of several of these reactions are listed in Table II.

Table II. The Benzoyl Peroxide Initiated Cyanation of Several Hydrocarbons with Cyanogen Chloride

$$RH + CNCl \xrightarrow{Bz_2O_2} RCN + RCl$$

Reactants	Products	Yield, %
Cyclohexane	Cyclohexyl cyanide	66
2,3-Dimethylbutane	α,α,β-Trimethylbutyronitrile	95
n-Butane	α-Methylbutyronitrile	50
	Valeronitrile	4
Neopentane	β,β-Dimethylbutyronitrile	45

Experimental Section

Materials. The hydrocarbons n-butane, neopentane, cyclohexane, and 2,3-dimethylbutane were Phillips research grade and were used without purification. Toluene and acetonitrile were obtained from Fisher Scientific Co. and were distilled from phosphoric oxide. Benzyl cyanide (J. T. Baker Chemical Co.) was distilled at atmospheric pressure. Cyanogen, cyanogen chloride, and hydrogen chloride were supplied by Matheson Co., Inc., and used without purification. Deuterium chloride (99%) was obtained from Merck Sharp and Dohme (Canada) Ltd. Perdeuteriocyclohexane (99.5%) was supplied by Stohler Isotope Chemicals.

Analytical. Hydrogen chloride (and deuterium chloride), cyanogen, and cyanogen chloride were all estimated volumetrically, cyanogen by absorption in sodium hydroxide solution followed by argentimetric determination of cyanide ion,[25] and cyanogen chloride by absorption in sodium sulfite solution and titration of the excess sodium sulfite against potassium permanganate solution.

The method was found to be a satisfactory volumetric method as follows. Measured volumes of cyanogen chloride were obtained using standard vacuum-line procedures and were condensed quantitatively into an ampoule containing a known quantity of sodium sulfite solution. The ampoule was sealed, allowed to thaw, and, after being shaken, opened, and the excess sodium sulfite was titrated against standard potassium permanganate solution. The results of five experiments gave a titrated value of 96 ± 3% of the measured volume of cyanogen chloride. It is important that the sodium sulfite should be freshly prepared; its titer begins to fall within 1 hr. This method has the advantage of rapidity and of being easy to carry out.

Glpc Analysis. The instruments used were an Aerograph Model 202 gas chromatograph equipped with a thermal conductivity detector and 10 ft × 0.25 in. stainless steel columns packed with an appropriate stationary phase (10%) on acid-washed Chromosorb W. This instrument could be used both analytically and for preparative work. For analytical work only, an Aerograph Hy-Fi Model 600D gas chromatograph, equipped with a flame-ionization detector, was also used. The columns used were 10 ft × 1/8 in. stainless steel packed with the materials described above.

Products were estimated by comparing their peak areas with those of an internal standard. The standard was calibrated against the authentic compound; peak areas were taken to be the product of the peak height and the width at half-height.

Mass Spectra. The instrument used was an A.E.I. Model MS9. Exact masses were determined by the use of standards of known mass. The deuteration experiments were analyzed by reducing the ionization voltage so that (M − 1)⁺ peaks were decreased in size

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compared with M⁺ as far as possible, without reducing the intensity of the spectrum so far that measurement of the peaks was inaccurate.

Procedure. Peroxide-initiated reactions were carried out in sealed Pyrex ampoules which had been degassed by a freeze–thaw method. The ampoules were allowed to stand in a constant-temperature bath for an appropriate period and were opened after being cooled to 77°K. When gaseous products were to be analyzed, they were fractionated on a vacuum line by standard procedures, with the aid of constant-temperature slush baths.[26] To analyze less volatile products, aliquots of the solution were estimated by glpc.

Photoinitiated reactions were carried out in quartz ampoules. The quartz was transparent down to about λ >200 mμ, which allowed the end absorption of cyanogen chloride[27] to be excited. The ampoules were sealed as described above, and irradiated at room temperature with a Hanovia L679A 450-W mercury arc. The lamp was cooled by being placed at the center of a water-cooled quartz immersion well, and the ampoules were placed near the outer edge of the immersion well.

After irradiation the analysis of the products was as described above. Products were collected by preparative glpc and were identified by comparison of their physical properties with those of authentic samples, where this was possible. All yields quoted are those estimated by glpc

The Reaction of Cyanogen Chloride with Cyclohexane. A degassed solution of cyanogen chloride (8.3 mmoles) and benzoyl peroxide (0.25 mmole) in cyclohexane (10 ml) was heated to 75° for 50 hr. Examination of the reaction mixture by glpc (SF96) revealed one major product (21%) which was found, after isolation by preparative glpc, to be cyclohexyl cyanide: nmr (CCl₄), τ 7.2–7.7 (broad singlet, 1 H), 7.9–8.9 (complex multiplet, 10 H); ir (CCl₄), ν 2240 cm⁻¹ (C≡N). *Anal.* Calcd for C₇H₁₁N: C, 77.00; H, 10.16; N, 12.83. Found: C, 76.48; H, 9.96; N, 13.00.

A series of reactions in which degassed 2.0-ml portions of a 0.70 M solution of cyanogen chloride in cyclohexane with varying quantities of benzoyl peroxide were heated to 98° for 3 hr indicated a chain length of 11 for the reaction (Bz₂O₂/ClCN < 0.06), and an optimum yield of cyclohexyl cyanide of 66% (Bz₂O₂/ClCN = 0.4). At the latter concentration of benzoyl peroxide a 15% yield of cyclohexyl chloride was also obtained. It was collected by preparative glpc and had an ir spectrum identical with that of authentic cyclohexyl chloride.

In a photochemical experiment a degassed solution of cyanogen chloride (10 mmoles) in cyclohexane (8 ml) was irradiated for 9 hr. The yield of cyclohexyl cyanide was 10%. When benzene (1.0 ml) was added as a photosensitizer to a similar mixture a yield of 25% was achieved. In neither case was cyclohexyl chloride a product (<0.3%).

The Reaction of Cyanogen Chloride with 2,3-Dimethylbutane. A degassed solution of cyanogen chloride (2.1 M) in 2,3-dimethylbutane (2.0 ml), in the presence of benzoyl peroxide (0.23 mmole), was heated to 75° for 97 hr. Analysis by glpc (SE30, 85°) indicated the presence of only two compounds. The first, 2-chloro-2,3-dimethylbutane (8%), isolated by preparative glpc, was identical (ir) with an authentic sample. The second, α,α,β-trimethylbutyronitrile (56%), was isolated and identified by its physical properties: nmr (CCl₄), τ 8.96 (doublet, J = 7 cps, 6 H), 8.85 (singlet, 6 H), 8.84 (septet, J = 7 cps, 1 H); ir (CCl₄), ν 2240 cm⁻¹ (C≡N).

A series of experiments, in which 2.0-ml samples of a 0.31 M solution of cyanogen chloride in 2,3-dimethylbutane were heated to 98° in the presence of varying quantities of benzoyl peroxide, gave an estimated chain length of 6 (Bz₂O₂/ClCN < 0.08), and an optimum yield of the alkyl cyanide close to 100%. The results of this experiment are shown in Figure 1.

Another series of reactions using varying amounts of benzoyl peroxide was carried out in benzene solution, with cyanogen chloride (0.23 M) and 2,3-dimethylbutane (0.23 M). It was found that the maximum yield of alkyl cyanide obtained was 35% and of alkyl chloride 33% based on hydrocarbon consumed. The "chain length" for production of the two compounds was 0.05.

In photochemical experiments, degassed samples (1.5 ml) of a 1.8 M solution of cyanogen chloride in 2,3-dimethylbutane gave a 30% yield of α,α,β-trimethylbutyronitrile after a 24-hr irradiation. The yield of 2-chloro-2,3-dimethylbutane was <0.5%. The yield

of alkyl cyanide was increased by the addition of benzene or of acetone to the reaction mixture.

The Reaction of Hydrogen Chloride with Cyclohexane. To a 0.73 M solution of hydrogen chloride (1.0 ml) in acetonitrile was added a 3.6 M solution of cyclohexane in acetonitrile (2.0 ml) together with varying amounts of benzoyl peroxide. The degassed mixtures were heated to 98° for 2 hr and then analyzed by glpc (SE30, 90°), and the product was isolated and identified (ir) as cyclohexyl chloride. The results of this experiment, which are seen in Figure 2, give an optimum yield for cyclohexyl chloride of 95%.

The Reaction of Cyanogen with 2,3-Dimethylbutane. To a sample of condensed cyanogen (0.6 ml) was added 2,3-dimethylbutane (10 ml). The solution was divided into two equal portions and to each was added benzoyl peroxide (0.05 g). The degassed solutions were heated to 98° for 3 hr and, on opening, each solution showed the same single peak on glpc (SE30, 125°). Preparative glpc (SE30, 125°) upon 8 ml of the solution allowed the isolation of α-imino-β,β,γ-trimethylvaleronitrile (I) (85 mg): nmr (CCl₄), τ 9.11 (doublet, J = 7 cps, 6 H), 8.87 (singlet, 6 H), 8.01 (septet, J = 7 cps, 1 H); ir (CCl₄), ν 1600 (C=N), 2210 cm⁻¹ (C≡N); after exchange with D₂O there was observed a new band at ν 2420 cm⁻¹ (N–D). *Anal.* Calcd for C₈H₁₄N₂: C, 69.57; H, 10.14; N, 20.29. Found: C, 69.21; H, 10.21; N, 19.73. The mass spectrum showed a small peak at m⁺/e 138 (M⁺), and a larger one at m⁺/e 125 (M − CH₃)⁺.

To the remaining 3 ml of the reaction mixture was added 5% sulfuric acid (4 ml) and the mixture was stirred for 1 hr at room temperature. Glpc (SE30, 125°) indicated the presence of a single compound of shorter retention time than the imino cyanide, and preparative glpc allowed the isolation of α-keto-β,β,γ-trimethylvaleronitrile (25 mg): nmr (CCl₄), τ 9.09 (doublet J = 7 cps, 6 H), 8.87 (singlet, 6 H), 7.88 (septet, J = 7 cps, 1 H); ir (CCl₄), ν 1700 (C=O), 2210 cm⁻¹ (C≡N).

Treatment of the above material with sodium hydroxide (0.5 g) in water (5 ml) heated to reflux for 1 hr gave, after extraction of the acidified solution, α,α,β-trimethylbutyric acid (9 mg): mp 41–45° (lit.[28,29] 42°, 50°); ir (CCl₄), ν 1695 (CO₂H), 3300–2500 cm⁻¹ (very broad, CO₂H); nmr (CCl₄), τ 8.28 (doublet, J = 7 cps, 6 H), 7.80 (singlet, 6 H), 6.04 (septet, J = 7 cps, 1 H), −2.25 (broad singlet, 1 H).

A series of experiments was carried out in which degassed solutions (2.0 ml) of cyanogen (0.08 M) in 2,3-dimethylbutane were heated to 98° for 3 hr in the presence of various amounts of benzoyl peroxide. The optimum yield of the imino cyanide was 70% (Bz₂O₂/C₂N₂ = 0.83), while at Bz₂O₂/C₂N₂ = 0.04 a chain length of 5 was found.

Photolysis of Cyanogen Chloride with 2,3-Dimethylbutane in the Presence of Deuterium Chloride. Duplicate samples of a solution of cyanogen chloride (0.27 M), deuterium chloride (0.35 M), and 2,3-dimethylbutane (0.46 M) in acetonitrile (1.7 ml) were degassed and irradiated for 4 hr. The reactions were analyzed by glpc (SE30, 65°) when the yield of α,α,β-trimethylbutyronitrile was found to be 11.8 ± 0.7% (0.055 ± 0.004 mmole). Isolation of the unreacted hydrocarbon by preparative glpc (Ucon Polar 50 HB 2000 (UP), 75°) and mass spectral analysis indicated that it contained a total of 0.052 ± 0.001 mg-atom of deuterium (9.1 ± 0.3%). The ratio of the number of exchanges to the number of molecules of alkyl cyanide formed was 0.96 ± 0.04.

In a control experiment, no incorporation of deuterium into the hydrocarbon resulted from the interaction of deuterium chloride (0.64 M) and 2,3-dimethylbutane (0.71 M) in acetonitrile (1.1 ml).

Photolysis of Cyanogen Chloride with Cyclohexane in the Presence of Deuterium Chloride. Duplicate samples of a solution of cyanogen chloride (0.33 M), deuterium chloride (0.44 M), and cyclohexane (0.49 M) in acetonitrile (1.9 ml) were degassed and irradiated for 4 hr. Glpc analysis (SE30, 110°) indicated the yield of cyclohexyl cyanide to be 0.070 ± 0.005 mmole (11.3 ± 0.8%). Isolation of the unreacted hydrocarbon and subsequent mass spectral analysis gave the incorporation of deuterium as 0.50 ± 0.02 mg-atom (60 ± 2%). The ratio of exchanges to formation of alkyl cyanide was 7.2 ± 0.8.

In a control experiment, when deuterium chloride (0.55 M) and cyclohexane (0.84 M) interacted in acetonitrile (1.1 ml), no incorporation of deuterium in the hydrocarbon was observed.

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The Photolysis of Cyanogen Chloride with a Mixture of Cyclohexane and Perdeuteriocyclohexane. A solution of cyanogen chloride (0.62 M), cyclohexane (0.97 M), and perdeuteriocyclohexane (0.83 M) in acetonitrile (1.9 ml) was degassed and irradiated for 4 hr. Glpc analysis (SE30, 110°) for (total) cyclohexyl cyanide gave a yield of 0.24 mmole (20.5%), and isolation of the unreacted hydrocarbon mixture (SE30, 70°) and analysis by the mass spectrum indicated that the cyclohexane contained 0.044 mg-atom of deuterium and that the perdeuterated material contained 0.051 mg-atom of hydrogen. The ratio of the number of exchanges to product formed was 0.84.

The reaction was repeated using a solution (1.6 ml) which was 0.72 M in cyanogen chloride and 0.35 and 0.30 M in cyclohexane and perdeuteriocyclohexane, respectively. An analogous analytical procedure showed that the yield of (total) cyclohexyl cyanide was 0.06 mmole (5.2%), of deuterium in the unreacted cyclohexane was 0.018 mg-atom, and of hydrogen in the perdeuteriocyclohexane was 0.008 mg-atom. The ratio of exchanges to formation of product was 0.86.

The Reaction of Cyanogen Chloride with n-Butane. To a solution of cyanogen chloride (0.30 M) and benzoyl peroxide (0.11 M) in acetonitrile (four 2.0-ml portions) was added n-butane (0.5 ml). The degassed solutions were heated to 98° for 3 hr. Glpc analysis for alkyl chlorides (UP, 70°), and for alkyl cyanides (UP, 125°) indicated the following yields: 1-chlorobutane, 0.3%; 2-chlorobutane, 6%; valeronitrile, 4%; α-methylbutyronitrile, 50%. The latter compound was isolated and identified by ir and nmr; the former three were identified by comparison of their retention times on glpc (UP and SE30) with those of authentic samples.

In a photochemical experiment a series of solutions of cyanogen chloride (3.3 M) in n-butane was degassed and irradiated for 2–6 hr. The products of the reaction were analyzed by glpc (UP, 115°). It was found that the ratio of valeronitrile to α-methylbutyronitrile varied according to the extent of the reaction. These results were summarized in Table I.

The Reaction of Cyanogen Chloride with Toluene. A solution of cyanogen chloride (8 mmoles) and benzoyl peroxide (0.27 mmole) in toluene (10 ml) was degassed and heated to 75° for 50 hr. Glpc analysis (neopentyl glycol succinate (NPGS), 190°) indicated the presence of benzyl cyanide (1.8%) and a sample was isolated by preparative glpc and identified by its ir.

Further experiments with a solution of cyanogen chloride (0.64 M) in toluene in the presence of varying quantities of benzoyl peroxide indicated that benzyl chloride was also formed. The optimum yield of benzyl cyanide was 10.8% ($Bz_2O_2/CNCl = 0.72$) and a "chain length" of 0.6 was found. The yield of benzyl chloride was always slightly less than that of benzyl cyanide. When the reaction of cyanogen chloride and toluene was photoinitiated, no benzyl cyanide could be detected.

The Photolysis of Chlorine with Benzyl Cyanide. A sample of benzyl cyanide was shown to be free of benzyl chloride and cyanogen chloride by glpc (SE30, NPGS). Chlorine was now bubbled into duplicate samples of the pure liquid (2.0 ml) in the dark until a saturated solution was obtained. The solutions were degassed and irradiated with light from an incandescent lamp in a Pyrex ampoule, until the color of chlorine had disappeared. The solution was now opened directly into the vacuum line and the products were fractionated[30] between three traps maintained at −63, −95, and −196°. Hydrogen chloride passed into the latter trap and was discarded. The contents of the −95° trap were analyzed for cyanogen chloride using the mass spectrometer, and an exact mass analysis showed the presence of cyanogen chloride in the peak at m^+/e 61 (calculated mass, 60.9720; found, 60.9719). Glpc analysis, using two columns (SE30, NPGS) of the residual liquid confirmed the presence of benzyl chloride in the mixture.

The Reaction of Cyanogen Chloride with Neopentane. A mixture of cyanogen chloride (10 mmoles), benzoyl peroxide (0.17 mmole), benzene (5 ml), and neopentane (4 ml) was degassed and heated to 75° for 51 hr. Glpc analysis (SF96, 85°) showed the presence of one product, of which a sample was collected by preparative glpc (SF96, 85°) and found to be β,β-dimethylbutyronitrile: nmr (CCl₄), τ 8.88 (singlet, 9 H), 7.85 (singlet, 2 H); ir (CCl₄), ν 2245 cm⁻¹ (C≡N).

A series of reactions was carried out in acetonitrile (1.0 ml) containing cyanogen chloride (0.73 mmole), to which was added neopentane (0.5 ml) and varying quantities of benzoyl peroxide. The optimum yield of β,β-dimethylbutyronitrile was 45% ($Bz_2O_2/ClCN = 0.9$).

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The Exchange Reaction of Acetyl Fluoride and Acetyl Hexafluoroarsenate[1]

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Abstract: From the temperature dependence of the exchange rate of the methyl protons between acetyl fluoride and acetyl hexafluoroarsenate an Arrhenius activation energy of 11.0 ± 0.4 kcal/mol and a preexponential factor of $10^{8.9 \pm 0.3}$ were obtained. From the concentration dependence of the exchange rate the reaction was found to be one-half order in acetyl hexafluoroarsenate and zero order in acetyl fluoride.

There have been many proton magnetic resonance studies of carbonium ions which are stable in solution.[3] Information about the rates of exchange processes has been obtained from variable temperature studies.[4] However, few investigations have been made

where the concentration of all exchanging species could be independently varied.[5] Such a procedure is advisable to determine the mechanism of the exchange reaction. Since the relatively unstable carbonium ions are usually prepared by dissolving the precursor in a very strongly acidic medium it has not been possible to control the relative concentrations of the exchanging species for these ions. In the present study it was

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