

## Cyano Transfer from Acetonitrile to Aromatic Compounds

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The reaction between acetonitrile and aromatic compounds in a 13.6-MHz, inductively coupled, rf discharge was studied. The two compounds to be reacted were simultaneously flowed through the reactor. The total pressure was about 0.05 torr. The flow rates (about 1 mmol/min) of each were independently controlled and varied as was the applied power. Aryl nitriles were major products from benzene, toluene, (trifluoromethyl)benzene, pyridine, thiophene, and naphthalene. Yields (5-g scale) based on reacted aromatic of 80% could be obtained with benzene, naphthalene, and pyridine. The isomer ratios from toluene, pyridine, thiophene, and naphthalene were nearly, but not exactly, statistical. Quantitative studies of the benzene-acetonitrile reaction showed the rate of disappearance of acetonitrile to be directly proportional to power and inversely proportional to total flow rate as expressed in a rate law. The rate of benzene conversion also depends on power and total flow rate, but larger rate constants were obtained with a larger mole fraction of acetonitrile. The yield of benzonitrile was proportional to the mole fraction of acetonitrile. Mechanistic implications are discussed.

The plasma generated by an rf discharge provides a unique reaction medium, and therefore the plasmolysis of organic compounds often produces unique transformations.<sup>1</sup> The technique is of some synthetic interest because selective reactions have been discovered and because one can easily produce grams of products in tens of minutes. In the sense that chemical synthesis means the construction of complex compounds from simpler ones, an especially interesting experiment is one in which two compounds are passed simultaneously through the plasma zone in the hope of coupling together these reactants or some fragments derived from them. There have been few experiments of this kind since the few investigators in this field have found the reactions from single compounds sufficiently complex. Recent experiments in our laboratory have, however, utilized the coplasmolysis of two reactants.<sup>2,3</sup> These and other experiments have provided some new insight into the kinetics of plasma reactions, and we felt that studies involving coplasmolysis could be profitably undertaken.

This paper results from the observation that the reaction kinetics for mixtures of acetonitrile and anisole were unusual. It was soon discovered that when benzene and acetonitrile were simultaneously flowed through the reactor, benzonitrile resulted. The unusualness of this reaction piqued our interest and prompted study both from a synthetic and a mechanistic viewpoint. The reaction between benzene and acetonitrile has been reported by Kikkawa and co-workers. They used an rf discharge with electrodes in the gas flow and obtained benzonitrile in yields of 5–10% based on reacted benzene.<sup>4</sup> A second paper reported the use of an inductively coupled discharge in which benzonitrile was produced in 10–15% yield.<sup>5</sup> The present study demonstrates that substantially higher yields can be obtained and extends the reaction to other aromatics and heterocyclic compounds. Reaction rates and product yields are quantitated and correlated using rate laws. This allows some mechanistic insight.

### Results

The apparatus is quite similar to that previously described.<sup>2</sup> The experiment involves simultaneously flowing acetonitrile and the aromatic through the plasma zone. The flow rates of the two compounds are independently controlled. Energy is supplied by an inductively coupled 13.6-MHz rf generator. The products are collected in a cold trap and eventually analyzed, usually by gas-liquid chromatography (GLC) and mass spectrometry (MS). The controlled variables are power ( $P$ ), flow rate of acetonitrile ( $r_A$ ), and flow rate of aromatic ( $r_B$ ). In general it was found that aryl cyanides were the major products. Qualitatively, the extent of conversion of reactants

depends directly on  $P$  and inversely on  $r$ . The yields of products are also dependent on  $P$ ,  $r_A$ , and  $r_B$ . It was established that no reaction occurs in the cold trap by coplasmolysis of benzene-acetonitrile with pyridine in the cold trap. No cyanopyridines resulted.

Results for the reaction of benzene-acetonitrile mixtures are contained in Table I. Benzonitrile was the major aromatic product, and it was formed in surprisingly high yield under the proper conditions. For example, in one run where 76% of the benzene reacted, a 61% yield of benzonitrile was produced. The yield, based on acetonitrile, was in this and all reactions with all aromatics less than 25%. In addition to benzonitrile, nonvolatile "polymer", toluene, and small amounts of biphenyl and toluonitriles were produced. The relative yields of these products change dramatically with the reaction conditions. In particular, benzonitrile is favored by a high  $r_A/r_B$  ratio. The three isomeric toluonitriles probably come from further reaction of initially formed toluene and/or benzonitrile since the yield of these isomers was highest under high conversion conditions. Interestingly, dicyanobenzenes were not observed as products.

The coplasmolysis of toluene and acetonitrile was performed similarly. The data are in Table II. The isomeric toluonitriles are major products formed in an ortho/meta/para ratio of 2.1:1.7:1.0. This ratio is independent of conditions. Bibenzyl, ethylbenzene, xylenes, and benzene are side products. These products are favored by low  $r_A/r_B$  and are also formed in a toluene plasmolysis in the absence of acetonitrile. Other coplasmolysis products are benzonitrile and smaller amounts of benzyl cyanide. Unfortunately, the material balance is too poor to allow much interpretation of the relative yields of these products. Indeed, the ArCN yields from toluene are not high under the best of conditions.

More limited studies of the other compounds have been undertaken. In each case, however, the major volatile products demonstrate that cyanation competes with methylation and reactions typical of the aromatic alone. Clean cyanations are found with pyridine and naphthalene, which are themselves somewhat less reactive when plasmolized alone. The isomeric cyanopyridines are formed in a 2-cyano/3-cyano/4-cyano ratio of 1.8:2.6:1.0. This ratio varies only slightly with experimental conditions. The ratio of 1-cyanonaphthalene/2-cyanonaphthalene varied from 1:1 to 2:1. Thiophene gave the two cyanothiophene isomers and some methylation. The ratio 3-cyano/2-cyano was 0.95. The ratio 3-methyl/2-methyl was 0.3.

Trifluorotoluene-acetonitrile mixtures did lead to cyanotrifluorotoluenes as identified by GC-MS and apparently in reasonable yield. Because the authentic isomers were not

Table I. Yields from Benzene-Acetonitrile Plasmolysis

$r_A$ , mmol h <sup>-1</sup>	$r_B$ , mmol h <sup>-1</sup>	P, W	A/A <sub>0</sub> <sup>a</sup>	B/B <sub>0</sub> <sup>b</sup>	yield, % <sup>c</sup>	
					PhCN	PhCH <sub>3</sub>
133	21	100	0.34	0.14	46	2
140	24	70	0.45	0.24	47	4
158	27	50	0.64	0.47	41	4
125	19	40	0.50	0.34	50	3
140	20	20	0.74	0.68	27	3
121	81	70	0.58	0.81	9	3
146	94	40	0.64	0.92	5	2
121	77	20	0.66	0.95	3	1
179	179	70	0.65	0.95	2	1
217	127	70	0.65	0.91	4.6	2
260	84	70	0.66	0.83	11	3
241	67	100	0.61	0.74	15	5

<sup>a</sup> Conversion of acetonitrile: A<sub>0</sub> = amount passed; A = amount recovered. <sup>b</sup> Conversion of benzene. <sup>c</sup> Yield was determined by GLC, based on the total amount of benzene passed through the reactor.

Table II. Yields from ArH-CH<sub>3</sub>CN Reactions

ArH	$r_A$ , mmol h <sup>-1</sup>	$r_B$ , mmol h <sup>-1</sup>	P, W	A/A <sub>0</sub> <sup>a</sup>	B/B <sub>0</sub> <sup>b</sup>	yield, % <sup>c</sup>		
						ArCN <sup>d</sup>	ArCH <sub>3</sub>	other
toluene	211	60	20	0.59	0.71	8	7 <sup>e</sup>	PhH (5), PhCN (1)
	149	44	40	0.54	0.52	13	11	PhH (7), PhCN (4)
	155	50	50	0.49	0.45	15	11	PhH (7), PhCN (6)
	156	44	70	0.35	0.19	22	11	PhH (10), PhCN (12)
	102	55	50	0.49	0.45	11	13	PhH (8), PhCN (4)
	276	43	50	0.52	0.50	19	7	PhH (7), PhCN (5)
311	234	50	0.79	0.51	5	6	PhH (5), PhCN (1)	
naphthalene	426	43	40	0.60	0.84	14	1	
	430	72	40	0.61	0.90	9	1	
	123	23	40	0.43	0.59	33	4	
pyridine	306	118	40	0.90	0.87	7	2	
	359	74	40	0.90	0.76	15	4	
	404	71	40	0.86	0.83	17	4	
thiophene	187	144	40	0.90	0.63	6	3	
	303	137	40	0.70	0.72	10	5	
	385	122	40	0.59	0.70	13	4	

<sup>a</sup> Conversion of acetonitrile: A<sub>0</sub> = amount passed; A = amount recovered. <sup>b</sup> Conversion of aromatic. <sup>c</sup> Yield was determined by GLC, based on the total amount of aromatic passed through the reactor. <sup>d</sup> Sum of ring-substituted isomers. Isomer ratios are in the text. <sup>e</sup> Sum of ethylbenzene and xylenes. The ratio of isomers is approximately 3:1 ethylbenzene/xylenes.

Table III. Yields of ArCN from ArH-CH<sub>3</sub>CN

ArH	ArH conversion, %	ArCN yield, % <sup>a</sup>
benzene	76	61
	32	85
toluene	81	21
	50	38
naphthalene	49	83
pyridine	18	80
thiophene	30	40

<sup>a</sup> Yields are based on reacted ArH; sum of isomers, where appropriate.

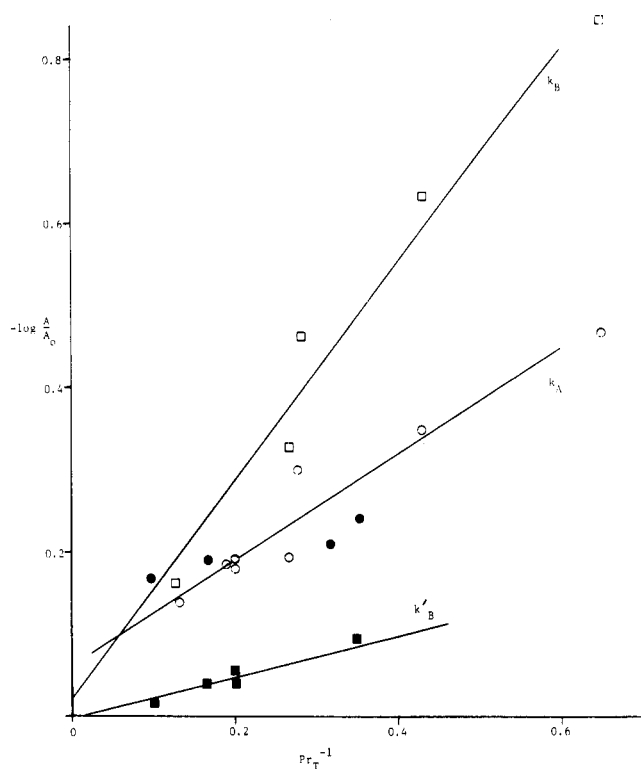
readily available to us and were not separated under the usual GLC conditions, this was not pursued further. The side products identified were fluorobenzene and benzonitrile. Two other substituted aromatics did not give any substantial amounts of ArCN. Chlorobenzene gives a variety of products including a small amount of ArCN. Phenol gives no evidence for ArCN products.

### Discussion

**Products.** The cyanation reaction is certainly unique, and this study demonstrates that it is effective with heterocyclic compounds as well as with simple aromatic hydrocarbons.

These reactions were performed on a scale of several grams. As demonstrated in Table III, respectable yields based on reacted aromatic can be obtained in several cases. These yields are improved by using a large ratio of acetonitrile/aromatic. In essence this demonstrates that acetonitrile, when present in excess, provides a reagent which rapidly and selectively transforms the aromatic to the nitrile, thus avoiding the usual plasma pathways of the aromatic. Similar selectivity based on one reactant has been shown in the plasmolytic formation of naphthalene from acetylene and styrene,<sup>6</sup> the trapping of benzyne from phthalic anhydride,<sup>7</sup> and the trapping of plasma generated trifluoromethyl radicals by certain metal halides.<sup>8</sup> It is an interesting approach to synthesis because the reagent in excess can be one which is usually inert, i.e., hexafluoroethane, acetonitrile, or acetylene.

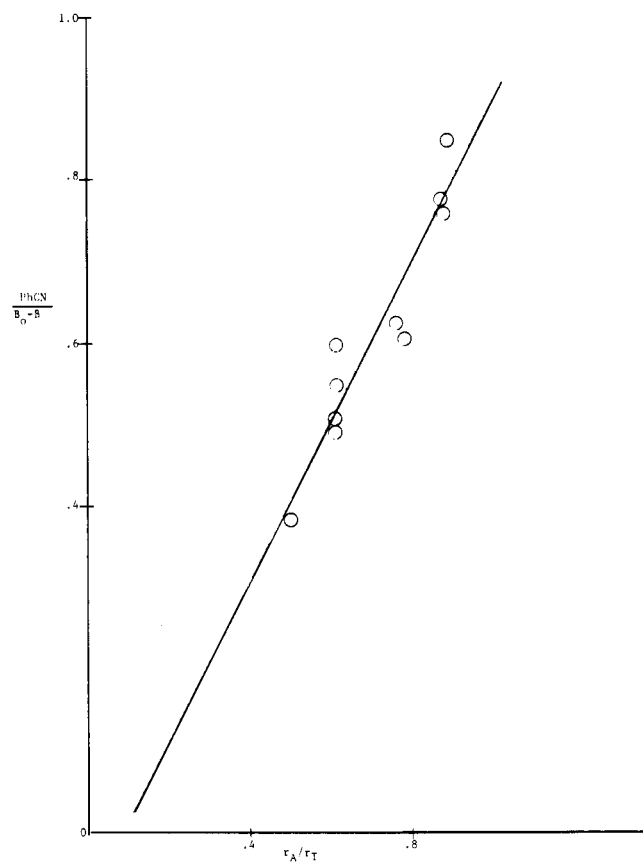
A comparison of efficiencies and isomer ratios with other direct cyanations is of interest. One method involves anodic oxidation of ArH-CN<sup>-</sup> mixtures and proceeds in good yield for electron-rich aromatics like anisole.<sup>9</sup> The second utilizes photolysis of ICN and is proposed to involve cyano radical (CN).<sup>10</sup> The mechanisms of these reactions seem different from each other based on the differing positional selectivities. Toluene gives a nearly statistical mixture of isomers in the photochemical cyanation (in solution), while the anodic process favors ortho-para substitution.<sup>10</sup> Neither of these reactions has been applied to pyridine, thiophene, or  $\alpha,\alpha,\alpha$ -tri-



**Figure 1.** Benzene-acetonitrile reaction rates: (○) acetonitrile at  $r_A/r_B \approx 6$ ; (●) acetonitrile at  $r_A/r_B = 1.0-1.6$ ; (□) benzene at  $r_A/r_B \approx 6$ ; (■) benzene at  $r_A/r_B = 1.0-1.6$ .

fluorotoluene. A comparison of positional selectivities on toluene then indicates that the plasma reaction is similar to ICN photolysis, and this could be accommodated by a radical mechanism involving  $\cdot\text{CN}$ . It must, however, be noted that other processes could also be unselective and that the photolysis mechanism has not been thoroughly studied. The competing plasma methylations are also of interest with regard to radical mechanisms. The reaction of thiophene-acetonitrile, for example, gives considerable amounts of methylthiophene, and the isomer ratios are quite reproducible. The ratio of 3-methylthiophene/2-methylthiophene is 0.3. In contrast, the cyanation ratio is 0.95. If, for example, the reaction involved electron impact generation of 2- and 3-thiophenyl radicals followed by combination with either  $\cdot\text{CN}$  or  $\cdot\text{CH}_3$  from  $\text{CH}_3\text{CN}$ , it would be expected that the 3/2 ratios would be quite similar. There are, of course, ways in which this simple expectation could be aborted, but it suggests that cyanation and methylation have different mechanisms. Strongly reinforcing this view is the fact that the benzonitrile/toluene ratio from benzene varies from 2 to 20 as conditions, especially  $r_A/r_B$ , are varied. Certainly a scheme whereby benzene produces phenyl and acetonitrile produces equal amounts of cyano and methyl radicals which then combine to give benzonitrile or toluene is ruled out.

**Kinetics.** Since some success has been recently achieved in resolving the dynamics of organic plasmolysis, we wish to apply this approach to the present, more complex, problem. Our efforts center on the cyanation of benzene. It has been previously shown<sup>2,3</sup> that the rates of several rf discharge reactions follow the rate law shown in eq 1. This rate law can be shown to be consistent with a scheme in which an initial electron impact on reactant is rate limiting or with other schemes which are essentially limited by energy input and are first order in reactant. In this situation the amount of reactant converted in a given run depends directly on the power and residence time and inversely on the total pressure of organic compounds.<sup>11</sup> This rate law can be tested for acetonitrile



**Figure 2.** Yield of benzonitrile based on reacted benzene vs. acetonitrile mole fraction.

conversion using the data in Table I. If all of the points are used, a linear regression analysis gives  $-\log(A/A_0) = 0.63Pr_T^{-1} + 0.08$ , where  $k$  is expressed in units of  $\text{mmol W}^{-1} \text{h}^{-1}$ . The standard deviation  $r = 0.93$ . Using only the points at  $r_A/r_B$  of approximately 6 (see below),  $k = 0.63 \text{ mmol W}^{-1} \text{h}^{-1}$  and  $r = 0.96$ . These rate constants are satisfactorily close to those previously estimated for acetonitrile alone using a similar reactor. Although the correlation coefficients are not high, there are no obvious trends with  $P$ ,  $r_A$ , or  $r_B$ , and in particular  $k$  is nearly independent of  $r_A/r_B$ .

$$-\log(A/A_0) = kP/r_T + C \quad (1)$$

The kinetics for disappearance of benzene are quite different. A linear plot for  $-\log(B/B_0)$  vs.  $Pr_T^{-1}$  is obtained for  $r_A/r_B \approx 6$  (Figure 1). The regression analysis gives  $-\log(B/B_0) = 1.32Pr_T^{-1} + 0.02$ ,  $r = 0.98$ . The rate constant so obtained is, however, much larger than that for benzene alone, and it depends on  $r_A/r_B$ . At  $r_A/r_B = 1.0-1.6$ , the rate constant is some 6 times smaller and is closer to the rate for benzene alone. It is proposed, therefore, that there are two main routes for consumption of benzene. One is direct plasmolysis to produce toluene, polymer, and other products with a rate which should be nearly independent of  $r_A/r_B$ . The other, the dominant route, acts to increase the rate constant for disappearance of benzene as  $r_A/r_B$  increases and leads to benzonitrile. The rate law for this reaction can be described as pseudo first order in benzene. Acetonitrile and benzene (or species derived from them) are both involved in the rate-limiting step.

The competition between the two pathways for benzene consumption can be quantitatively expressed in terms of the relative yield of benzonitrile. As shown in Figure 2, the yield of benzonitrile based on benzene consumed is linearly related to  $r_A/r_T$ . Thus, benzonitrile formation and the benzene rate enhancement are both the result of one mechanistic phe-

Table IV. Peak Intensities from CIMS

reactant (%)	V	pressure, torr	m/e	peak intensity						
				42	54	83	95	78	91	118
CH <sub>3</sub> CN (100)	130	0.2		63	5	2.5	0.4			
CH <sub>3</sub> CN (99)-C <sub>6</sub> H <sub>6</sub> (1)	130	0.18		290	20	30	3	77	7	3.6
CH <sub>3</sub> CN (98)-C <sub>6</sub> H <sub>6</sub> (2)	25	0.15		4	4	400	43	37	1	2.5

nomenon. An alternative explanation for the benzene rate enhancement would involve increasing the electron energies or density as acetonitrile is added. This would, however, account for neither the change in products nor the lack of dependence of the acetonitrile rate on  $r_A/r_B$ .

No evidence is available which defines the structure of the reactive intermediates involved in cyanation. These could in principle be radicals, ions, or excited species. It has been shown spectroscopically that  $\cdot\text{CN}$  is produced from acetonitrile in an rf plasma,<sup>14</sup> and indeed this is a well-characterized species from plasmas<sup>15</sup> and from acetonitrile photolyses.<sup>16</sup> The reactivity of  $\cdot\text{CN}$  has been probed by pulse radiolysis of NC-CN vapor.<sup>17</sup> It was found that  $\cdot\text{CN}$  reacted with benzene with  $k = 1.7 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and ethane with  $k = 1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 300 °C. Unfortunately, the products were not well characterized. The rapid reaction with ethane, an aliphatic hydrocarbon, prompted studies of the coplasmolysis of cyclohexane and acetonitrile.<sup>18</sup> No cyanocyclohexane or the isocyanide was formed under a variety of conditions similar to those reported here, where both compounds were reacting. We note that this result is similar to the low yields of benzyl cyanide from toluene. It may be that  $\cdot\text{CN}$  does not lead to such aliphatic substitution products<sup>19</sup> or that another intermediate is involved.

Phenyl radicals have likewise been proposed as intermediates from benzene in an rf discharge based on experiments which benzene and deuterium gas were coplasmolized to give deuteriobenzene.<sup>12</sup> A similar observation has been made by Tezuka,<sup>13</sup> who studied the plasmolysis of benzene-*d*<sub>1</sub> and found considerable amounts of benzene-*d*<sub>0</sub> and -*d*<sub>2</sub> in the recovered reactant.

A variety of ionic species are also acceptable a priori intermediates. The comparative ion chemistry has been probed here using ion cyclotron resonance and mass spectrometry.<sup>20</sup> Of particular interest is the ICR study of mixtures of benzene and acetonitrile.<sup>21</sup> It was found by double resonance that  $m/e$  42 ( $\text{CH}_3\text{C}^+\text{NH}$ ) reacted with benzene to give  $m/e$  118 ( $\text{C}_6\text{H}_5\text{NCCH}_3^+$ ). No evidence for  $m/e$  103 benzonitrile or protonated benzonitrile was found. This was affirmed by W. Farneth at the University of Minnesota. Chemical ionization mass spectrometry (CIMS) might be especially pertinent to plasma reactivity because the pressures are quite similar. This is a facet not properly emphasized in previous comparisons of MS and plasma chemistry. Typical CIMS conditions used here were 25- or 130-eV ionizing voltages and 0.1–0.3 torr pressures. Data are collected in Table IV. The spectrum of acetonitrile alone shows intense peaks at  $m/e$  42 and 83, corresponding to protonated acetonitrile and a protonated dimer ( $\text{CH}_3\text{CN}-\text{H}-\text{NCCH}_3^+$ ), respectively. The next most intense peaks are  $m/e$  54 and 95. The relative intensities of these two peaks are quite variable. Low ionizing energies and high pressures favor  $m/e$  83 over 42. Spectra resulting from electron bombardment of 99:1 acetonitrile/benzene mixtures showed new peaks at  $m/e$  78, 91, and 118. These peaks correspond to benzene<sup>+</sup>, benzyl cation (tropylium), and an adduct composed from benzene and  $^+\text{CH}_2\text{CN}$ , respectively. A peak at  $m/e$  104 corresponding to protonated benzonitrile is always present, but its intensity is typically 20% of that at  $m/e$  118. Thus, the ionic chemistry observed by CIMS bears only a faint resemblance to the observed cyanation. It should, however,

be realized that one is observing only ionic products in the CIMS and this could be misleading.

In general it must be true that an understanding of plasma reactions can only come from direct studies, and not from comparisons with other chemistry. Our work has centered on providing a kinetic description. This will hopefully provide a framework within which the nature of the intermediates can be elucidated. Indeed, the present mechanistic problem could succumb to a careful combination of spectroscopic and physical organic methods.

### Experimental Section

All reactants were commercial samples used without purification. Authentic samples of products were also purchased.

Plasmolysis experiments were carried out in a double-walled reactor tube (30 × 2.5 cm i.d.) heated by circulating thermostated silicone oil through the jacket. The wall temperature was held at 110 °C except for the benzene reactions which were conducted at 100 °C. The naphthalene and phenol reactions were performed in a different apparatus in which the heating jacket extended around one reactant reservoir. This is especially useful for compounds with low vapor pressures. The glow discharge was generated by an rf generator at 13.56 MHz (Tegal Model 100) with inductive coupling (copper coil, 10 turns in 8 cm) through a tunable Collins filter. The applied "forward" power was estimated with a built-in wattmeter. Reflected power was zero. Acetonitrile and the aromatic compound were contained in separate reservoirs. The flow rate of each was controlled by the temperatures of the reservoirs and adjustable needle valves. Mixing took place above the entrance into the plasma zone. Flow rate was determined by weighing the reactant reservoir before and after the run and measuring the elapsed time. The mixtures were distilled through the plasma zone at pressures of about 0.05 torr. The pressure varied with the flow rate. The residence time in the plasma zone was about 0.1 s. Products and nonreacted starting materials were frozen out in a liquid nitrogen cooled trap, which was located immediately (5–10 cm) beyond the plasma zone.

Analyses of products were carried out by temperature programmed GLC and GLC-MS on columns (1 or 3 m × 1/8 in.; 10% silicone gum rubber SE-30 on Chromosorb W NAW, 80–100 mesh). All products were identified by GLC by comparison with authentic compounds and further comparison of mass spectra.

CIMS experiments were performed on a Finnegan Model 4000 instrument.

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**Registry No.**—Benzene, 71-43-2; toluene, 108-88-3; naphthalene, 91-20-3; pyridine, 110-86-1; thiophene, 110-02-1; acetonitrile, 75-05-8; benzonitrile, 100-47-0; *o*-toluonitrile, 529-19-1; *m*-toluonitrile, 620-22-4; *p*-toluonitrile, 104-85-8; 2-cyanopyridine, 100-70-9; 3-cyanopyridine, 100-54-9; 4-cyanopyridine, 100-48-1; 1-cyanonaphthalene, 86-53-3; 2-cyanonaphthalene, 613-46-7; 3-cyanothiophene, 1641-09-4; 2-cyanothiophene, 1003-31-2.

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## Free-Radical Cyanation. Novel Free-Radical Reaction of Methyl Cyanofornate or Cyanogen with 2,4-Dimethylpentane

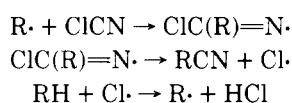
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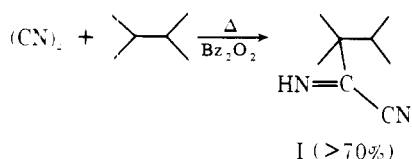
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The peroxide-initiated free-radical chain cyanation of several hydrocarbons with methyl cyanofornate has been observed. The reaction is proposed to proceed through the intermediacy of an iminyl radical formed from the addition of an alkyl radical to the carbon-nitrogen triple bond. The resulting iminyl radical undergoes  $\beta$ -scission to form the alkyl cyanide (>70%), carbon dioxide, and a methyl radical which subsequently carries the chain. Only traces of products possibly arising from carbonyl addition were observed. The peroxide promoted reaction of the reagent with 2,4-dimethylpentane yielded only minor amounts of the three possible cyanides (20%), but gave as the major product in 55% yield the difunctionalized cyclic hydrocarbon, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene. The reaction pathway for the formation of the cyclized product proceeds by addition of the first formed tertiary alkyl radical to the cyano triple bond to form the iminyl radical, the same radical used to rationalize the chain cyanation; internal hydrogen abstraction by the iminyl radical formed from this addition (six-membered ring transition state), followed by addition of the new tertiary radical to the nitrogen of the imine double bond (five-membered ring transition state) and disproportionation of the new radical to yield the difunctionalized cyclic product in a nonchain process. Consistent with this mechanism was the observation that a modest yield (22%) of difunctionalized cyclic product, 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene, was formed by the nonchain reaction of cyanogen with 2,4-dimethylpentane.

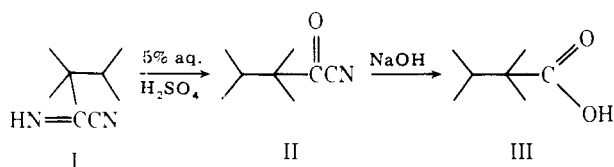
Cyanogen chloride was shown to undergo an initiated free-radical chain cyanation reaction with a variety of hydrocarbon substrates.<sup>1</sup>



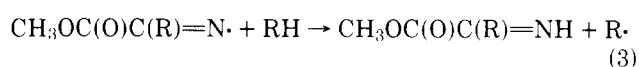
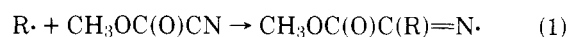
In the course of this investigation we reported that cyanogen underwent an initiated chain reaction with 2,3-dimethylbutane to give an exceptionally high yield of a single substitution product, I. The iminocyanide (I) could be quantitatively



converted by hydrolysis to its acyl cyanide (II) or its carboxylic acid (III).



The selective homologation of a hydrocarbon by one or two functionalized carbon atoms has some potential synthetic utility. The cyanation reaction with cyanogen chloride was successful, but unfortunately the reaction with cyanogen failed when tried with a large number of other substrates.<sup>2</sup> In an attempt to find yet another cyanating reagent (sequence 1, 2, 4) or to find a general method to synthesize the intermediate acyl cyanide (via carbonyl addition- $\beta$ -scission) or its hydrolytate, the keto acid, in mechanistically analogous manners (sequence 1-3 followed by hydrolysis) the reactions of a number of hydrocarbons with methyl cyanofornate were attempted.



### Results and Discussion

Solutions of methyl cyanofornate (0.235 M) and benzoyl peroxide (10-24 mol %) in 2,3-dimethylbutane were heated in sealed degassed reaction tubes at 99 °C for 5.5 h. One major product was detected (GLC) which resulted from the reaction of methyl cyanofornate and 2,3-dimethylbutane,  $\alpha,\alpha,\beta$ -trimethylbutyronitrile (IV). The product appears to be formed by a short chain process, since an optimum yield (77%) was