

## The Ambident Nature of the Cyanide Ion

### The Reaction between Trityl Chloride and Tetraphenylarsonium Cyanide in Acetonitrile

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Trityl chloride and tetraphenylarsonium cyanide react in acetonitrile to yield both trityl isonitrile and trityl cyanide. Trityl perchlorate gives the same product ratio at 25°C as does trityl chloride, namely 10 % isonitrile and 90 % cyanide. It is therefore suggested that the free dissociated carbonium ion is the reacting species, which is trapped by the cyanide ion.

From product analysis of the reaction performed at 3 different temperatures, -17°C, +25°C, and 81.5°C, the energy of activation for trapping of the carbonium ion by the nitrogen end of the cyanide ion is calculated to be  $1.8 \pm 0.3$  kcal mol<sup>-1</sup> higher than for trapping by the carbon end.

Titration with bromine in carbon tetrachloride, of an organic isonitrile in the presence of an organic cyanide, has been found to be a valuable analytical method for the quantitative determination of the isonitrile.

In 1955, Kornblum<sup>1</sup> introduced the concept of ambidence for anions possessing two different reactive atoms. Later, this idea has been applied with success to the chemistry of cations,<sup>2</sup> and more generally to nucleophiles and electrophiles.<sup>3</sup> Several reviews have appeared.<sup>4-7</sup> The necessary distinction, however, between thermodynamic and kinetic ambidence has been largely neglected.

One of the ions originally suggested by Kornblum<sup>1</sup> as an ambident ion was the cyanide ion. The reason was that it had been known for a long time that several heavy metal cyanides, especially silver cyanide, in appropriate non-hydroxylic solvents<sup>8-10</sup> react with alkyl halides, preferably S<sub>N</sub>1 type alkyl iodides,<sup>1</sup> to yield isonitriles in rather good yields, while alkali cyanides yield the alkyl cyanides. According to Kornblum,<sup>1</sup> the presence of silver ions will enhance the carbonium character of the transition state, and favour reaction with the end of the cyanide ion which has highest electron density.

It is now known that it is the carbon atom of the cyanide ion which is most electron-rich,<sup>11</sup> and the yield of isonitriles with heavy metal cyanides

is not only due to a simple abstraction of the halide creating a carbonium ion. The isonitrile is probably formed *via* a metal cyanide-alkyl halide complex,<sup>12-16</sup> as a consequence of the increased basicity of the nitrogen end of the cyano group arising from the metal-carbon coordination in the metal cyanide complex.<sup>17</sup>

From Purcell's extensive studies<sup>17</sup> on the cyano group, where the effect on the nitrogen lone pair of coordination through the carbon atom has been particularly stressed, it is not surprising that the nitrogen atom of carbon-coordinated cyanides readily takes part in bond formation. Thus, several metal and non-metal cyanides are polymers,<sup>18</sup> hydrogen cyanide itself is hydrogen bonded with a rather short  $\text{H}\cdots\text{N}$  distance, 3.18 Å,<sup>19</sup> and a number of bridged cyanide complexes have been isolated<sup>20</sup> or proven as intermediates.<sup>21</sup> Recently, cyano complexes of silver<sup>12</sup> and copper<sup>22</sup> have been found to be valuable reagents for the synthesis of organic isonitriles. Shriver<sup>23</sup> has published a comprehensive article on the bifunctional behaviour of the cyano group.

With regard to Kornblum's<sup>1</sup> original definition of an ambident anion, it seems now, especially in view of Purcell's<sup>17</sup> findings on the basicity of the nitrogen end and its dependence upon coordination to carbon, and also on the basis of extensive experimental evidence, that the concept of ambidence has been used in cases where the actual ambidence has been forced upon the cyano group by carbon coordination, or has been enhanced by carbon coordination. We therefore tentatively suggest that the concept of ambidence should be used for ions and groups exhibiting ambifunctional behaviour in their free state only.

Still, there is no doubt that the cyanide ion is able to react by the nitrogen end. In many of the standard textbooks on organic chemistry, the ambident nature of the cyanide ion is stressed. This may, of course, be due to Nef's isonitrile synthesis with metal cyanides,<sup>8</sup> but several authors have claimed that traces of malodourous by-products are formed in the synthesis of alkyl cyanides from alkali cyanides and alkyl halides. To the best of the authors' knowledge, no quantitative study has ever been performed to evaluate the extent of isonitrile formation, or to work out exact procedures favouring nitrogen attachment to the organic group. On the other hand, several authors have noted that for typical  $\text{S}_{\text{N}}2$  reactions on aliphatic substrates, namely the reaction of cyanide ion with methyl halides in water,<sup>24</sup> and the decomposition of trimethylsulfonium cyanide in methanol and ethanol,<sup>25</sup> the only product obtained is acetonitrile. Martin and Weise,<sup>26</sup> however, has found that alkyl isonitriles as well as alkyl cyanides are formed in the reaction between aryl cyanates and trialkyl phosphites in benzene, presumably by decomposition of the suggested intermediates, trialkoxy aryloxyphosphonium cyanides. No relative yields were given. Compared with the decomposition of the sulfonium salts in alcohols,<sup>25</sup> the change of solvent may be the cause of the difference.

Recently, Kuroda and Gentile<sup>27</sup> have claimed the formation of discrete *cis*- $\alpha$  and *cis*- $\beta$   $\text{Co}[(\text{NC})_2 \text{ trien}]\text{ClO}_4$  from respectively *cis*- and *trans*- $\text{Co}[(\text{AcO})_2 \text{ trien}]\text{ClO}_4$  and sodium cyanide in water. Their structural interpretation<sup>27</sup> of the electronic and vibrational spectra, and therewith the identity of the products, has, however, been challenged.<sup>28</sup> Burmeister<sup>7</sup> has discussed the possible formation and stability of discrete isocyano complexes. Birk and

Espenson<sup>29</sup> estimated the isomerization energy of  $\text{Cr}[(\text{H}_2\text{O})^+\text{NC}]^{2+}$  to be very small. The lack of clearly proven cases of stable isocyano complexes may thus be due to their thermodynamic instability relative to the isomeric cyano complexes or bridged complexes, and not necessarily due to an overwhelming nucleophilicity of the carbon end of the cyanide ion compared with the nitrogen end. The need for differentiation between thermodynamic and kinetic ambivalence should again be stressed.

The electronic structure and the charge distribution of the cyanide ion has been the subject of several theoretical studies in the last few years. Wagner,<sup>30</sup> using the LCGO method, calculated the charges on the nitrogen and carbon atoms to be  $-0.25$  and  $-0.75$ , respectively. Shriver and Posner<sup>11</sup> found the highest filled orbital to have  $\sigma$  symmetry, being most localized on the carbon atom, and therefore primarily responsible for the basicity of the cyanide ion, while the next lower orbital was more localized on nitrogen. Bonaccorsi *et al.*,<sup>31</sup> however, calculated the center of charge of the three equivalent banana type orbitals to be closer to the nitrogen atom than to the carbon atom. Doggett and McKendrich<sup>32</sup> found the atomic charge on the nitrogen atom for an interatomic distance of  $1.159 \text{ \AA}$  to be  $-0.59$  by equipartitioning of overlap densities, and  $-0.64$  by asymmetric partitioning of overlap densities. The charge distribution in the cyanide ion was found by Doggett and McKendrich<sup>32</sup> to be rather insensitive to the small variations in  $\text{C}\equiv\text{N}$  bond lengths found experimentally.<sup>33</sup> Interestingly, recent determinations of the charge on the nitrogen atom of the cyanide ion, from the established relation between the observed position of the  $1s$  line in the electron spectrum (ESCA) and atomic charge on nitrogen, give charge values of  $-0.45$ <sup>34</sup> and  $-0.52$ .<sup>35</sup> Thus, one may conclude that the charge on the cyanide ion is roughly equally partitioned between the carbon atom and the nitrogen atom, the former atom having the higher sigma density in agreement with Shriver's original calculations.<sup>11</sup>

This equal partitioning of charge between the carbon atom and the nitrogen atom of the cyanide ion makes it necessary to examine which electrophilic centers are likely to be attacked by the carbon end of the cyanide ion, and which are likely to be attacked by the nitrogen end. The HSAB principle has been used with considerable success in rationalizing the reactivity pattern of ambident anions.<sup>3</sup> From the general experience that carbon nucleophiles are soft, as are carbanions, and nitrogen nucleophiles are hard, although the hardness is less pronounced when the nucleophilic nitrogen atom is part of a polarizable aromatic system as in pyridine, one may consider the carbon end the softer end, and the nitrogen end the harder end of the cyanide ion. In order to investigate the reactivity of the nitrogen end of the cyanide ion, one thus should choose an electrophilic center of exceptional hardness, which, as well, will give an isonitrile of sufficient stability.

As mentioned previously, metal isocyano complexes are of low thermodynamic stability, and so are silicon isonitriles.<sup>36</sup> This leaves, at present, carbon as the best example. Although  $\Delta G$  for the gas phase isomerization of alkyl isonitriles is  $-15 \text{ kcal/mol}$ , the isomerization is exceedingly slow at room temperature.<sup>37</sup>

The hardest possible carbon atom is that of the carbonium ion. Furthermore, it is known that by replacing hydrogen atoms in  $\text{CH}_3^+$  by methyl groups, one gets a progressively harder carbonium ion. From the order of stability of the isomeric butyl alcohols, the rule is that the more branched carbonium ion is the harder one.<sup>38</sup> For the ambident thiocyanate ion, values of the rate ratio  $k_S/k_N$  of a few units were determined for the reaction with carbonium ions,<sup>39</sup> while for direct displacement reactions on a primary substrate, the rate ratio  $k_S/k_N$  has been found to be 1300.<sup>40</sup> For this reason, trityl chloride was used as substrate in this work, to favour reaction with the nitrogen end of the cyanide ion.

Due to the high  $pK_a$  value of hydrogen cyanide in water, 9.19 at 26°C,<sup>41</sup> the effects of hydroxide and alkoxide ions can never be neglected when studying the cyanide ion in protic solvents. The alkoxide and hydroxide ions will often compete with the cyanide ion and favour reactions with hard centers, yielding products specific for these ions. Furthermore, the yield of triarylmethyl ethers and no triarylmethyl cyanides from triarylmethyl halides and potassium cyanides in methanol<sup>42</sup> suggests that a special reaction mechanism is favoured over the usual  $S_N1$  mechanism. The methoxide ion is probably not several powers of ten more reactive toward a triarylmethyl carbonium ion than is the cyanide ion.

These difficulties may be circumvented by working in dipolar aprotic solvents. As particularly stressed by Parker (Ref. 43 and references therein), a far better picture of an anion's nature and reactivity may be obtained from studies in dipolar aprotic solvents. Due to the very low solubility of alkali cyanides in dry dipolar aprotic solvents,<sup>42</sup> one is left with onium salts as the source of the cyanide ion in this class of solvents. As tetraalkylammonium cyanides are very hygroscopic and unpleasant to handle, tetraphenylarsonium cyanide seems to be the most convenient source of the cyanide ion in aprotic solvents.<sup>44-45</sup>

With regard to the solvent used in this work, acetonitrile, this solvent was chosen due to its well-known versatile nature.<sup>46</sup> Furthermore, the purification procedure for this solvent is well established.<sup>47</sup> Acetonitrile is a solvent of very low proton donating ability, combined with a medium dielectric constant, and possessing a medium donicity toward antimony pentachloride.<sup>48</sup> Nitromethane has been found to give trace of HCl with trityl chloride.<sup>49</sup> Finally, acetonitrile was found to be an excellent solvent for crystallization of both of the reactants, tetraphenylarsonium cyanide and trityl chloride.

The results of product ratio experiments are found in Table 1.

From colorimetric studies, Gutman<sup>51</sup> has concluded that trityl chloride is not ionized in acetonitrile. No conductivity experiment in this solvent, however, seems to have been performed. As trityl perchlorate, which is known to be extensively dissociated in less polar solvents than acetonitrile,<sup>52</sup> gives the same product ratio of trityl isonitrile and trityl cyanide at 25°C as does trityl chloride, one may conclude that the trityl carbonium ion is the reacting species.

The yield of trityl isonitrile is seen to increase with increasing temperature. From the product ratio of the reaction at the three temperatures, the energy of activation for trapping of the carbonium ion by the nitrogen end of the

Table 1. Yields of isonitrile and nitrile in the reaction,  $\text{RX} + \text{Ph}_4\text{AsCN} \rightarrow \text{RNC} + \text{RCN}$ , in acetonitrile.

RX	Temp. °C	Yield in %	
		RNC	RCN
MeI	25	0	100 <sup>a</sup>
Ph <sub>3</sub> CClO <sub>4</sub>	25	10	90
Ph <sub>3</sub> CCl	-17	6	92
Ph <sub>3</sub> CCl	25	10 <sup>b</sup>	88 <sup>c</sup>
Ph <sub>3</sub> CCl	81.5	17	80
Ph <sub>3</sub> CCl + LiClO <sub>4</sub> (1 : 1)	-25	0	100

<sup>a</sup>  $k_2(\text{MeCN}) = 26.5 \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_2(\text{MeOH})^{50} = 6.45 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ , thus  $k_2(\text{MeCN})/k_2(\text{MeOH}) = 4.1 \times 10^4$ .

<sup>b</sup>  $\nu_{\text{CN}}(\text{CCl}_4) = 2126 \text{ cm}^{-1}$ ,  $\Delta\nu_3 = 11 \text{ cm}^{-1}$ ,  $A = 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$ .

<sup>c</sup>  $\nu_{\text{CN}}(\text{CCl}_4) = 2239 \text{ cm}^{-1}$ ,  $\Delta\nu_3 = 8 \text{ cm}^{-1}$ ,  $A = 5.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-2}$ .

cyanide ion is found to be  $1.8 \pm 0.3 \text{ kcal mol}^{-1}$  higher than for trapping by the carbon end. The thermodynamically more stable product is thus also the kinetically preferred product, suggesting that the transition state occurs late in the reaction process.<sup>53</sup>

The presence of lithium perchlorate in the reaction between trityl chloride and tetraphenylarsonium cyanide is seen to completely depress the formation of trityl isonitrile, suggesting that hard Lewis acids, such as small metal ions, change the nucleophilic nature of the cyanide ion in dipolar aprotic solvents. From analogy with the proton (*cf.* the structure of hydrogen cyanide), one might anticipate that small metal ions associate to the carbon end of the cyanide ion and thus cause an increased reactivity of the nitrogen end of the cyanide ion. This view is, however, greatly oversimplified, as protonation of the cyanide ion through the carbon end is due to a special stabilization of both the  $\sigma$  bonding and the  $\pi$  bonding of the cyano group.<sup>17</sup> There are no theoretical calculations suggesting that the same effect necessarily is obtained with small alkali ions.

On the contrary, several pieces of evidence indicate that in lithium cyanide, the bond between the metal and the cyano group is *via* the nitrogen end. X-Ray studies by Bijovet<sup>54,55</sup> on cyanide salts show that in lithium cyanide, the Li-N distances are 2.06 Å and 2.19 Å, and the Li-C distance is 2.11 Å, while in ammonium cyanide, the H<sub>4</sub>N-C distance is 3.02 Å, considerably shorter than the H<sub>4</sub>N-N distance of 3.56 Å. Recently Bak,<sup>56</sup> using an all-electron SCF-LCAO-MO method, has calculated LiNC to be 9-10 kcal/mol more stable than LiCN in the gas phase. Furthermore, the fact that lithium cyanide as a cyaniding agent in non-polar solvents yields only organic cyanides and no organic isonitriles,<sup>57</sup> suggests a lithium-cyanide interaction *via* the nitrogen end of the cyano group. This may as well be the reason why 95 % of the charge of the cyanide ion in lithium cyanide is calculated to reside upon the nitrogen atom.<sup>58</sup> Thus one may conclude that lithium cyanide exists as lithium isonitrile.

Recently<sup>59</sup> it was shown that small alkali ions associate to the thiocyanate ion and the selenocyanate ion in dipolar aprotic solvents *via* the nitrogen ends of these ions, to cause a pronounced effect on the electronic distribution in these pseudohalide ions. Cation association creates a shift in the charge density toward the acceptor's site, similar to what occurs in the case of, *e.g.*, the phenoxide and nitronate ions.<sup>60</sup> Cation association is found to be sufficient to favour carbon alkylation in the reaction between phenoxide ions and alkyl halides.<sup>61</sup> Kurz *et al.*<sup>62</sup> have shown that the yield of *O*-alkylation product in alkylation reactions of ethyl acetoacetate increases when the cation is varied through the series  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{NR}_4^+$ . When examining the reactivity of the harder reactive center of an ambident anion, small metal ions should therefore be avoided.

Due to the solvation of anions in protic solvents, the effect of cation association upon the reactivity of ambident ions will be of minor importance in protic solvents, compared with the effect of the hydrogen-bonded solvation sphere surrounding the anions. The high reactivity ratio of the cyanide ion toward methyl iodide,  $4.1 \times 10^4$ , in acetonitrile and methanol as solvents, is characteristic for small ions with a relatively localized charge which should be strongly solvated in protic solvents.<sup>43</sup>

This view of the solvation of the cyanide ion is contrasted by the strongly positive partial entropy of the cyanide ion in water, 28.2 e.u.,<sup>63</sup> characteristic of an anion not acting as a strongly ordering one.<sup>64</sup> Ahrlund<sup>65</sup> has suggested that the cyanide ion is an even more pronounced structure breaker in protic solvents than is the iodide ion. This indicates that the charge on the cyanide ion is far less localized than anticipated, which is in accordance with the theoretical calculations. Furthermore, the increase of the nucleophilicity of the cyanide ion in going from protic solvents to dipolar aprotic solvents may be due to a very special solvation of the cyanide ion in protic solvents. Symons<sup>66</sup> has suggested that the solvation of the cyanide ion in methanol is asymmetric, hydrogen bonding being preferred along the bond axis.

Undoubtedly, the solvation sphere surrounding the cyanide ion will reduce the nucleophilicity of both ends of the cyanide ion in protic solvents compared to aprotic solvents, regardless of which way the solvent molecules are bonded to the cyanide ion. The question arises which end of the cyanide ion is most influenced by the solvation sphere in protic solvents, and how protic solvents will change the ambident nature of the cyanide ion compared to aprotic solvents. As shown by Ritchie *et al.*,<sup>42</sup> triarylmethylcarbonium ions cannot be used as substrates for examining the reactivity of the cyanide ion in alcohols, probably due to a special mechanism in this medium. In the case of other electrophilic centers, the choice of solvent, protic or aprotic, may be of crucial importance in direct synthesis, provided discrete inorganic isocyano complexes of, for example, hard metal ions are stable.

The exceptional ability of the carbon end of the cyanide ion to make strong bonds with both hard and soft Lewis acids is well known.<sup>64,65</sup> It is emphasized in this work that also the nitrogen end of the cyanide ion may make strong bonds with the lithium ion, indicating that small cations behave differently from the proton toward the cyanide ion. Using the HSAB principle, one may conclude that in protic solvents, the solvation sphere is more strongly

bonded to the nitrogen end, making the cyanide ion appear as a carbon nucleophile in protic solvents, and not as an ambident nucleophile. Further studies on the solvation of the cyanide ion in protic solvents may clarify this point. The results reported here suggest that the use of onium cyanides in dipolar aprotic solvents, or non-polar solvents,<sup>26</sup> is a necessary condition for the nitrogen end of the cyanide ion to be able to compete with the carbon end for hard electrophilic centers.

## EXPERIMENTAL

**Solvents.** Acetonitrile, "Baker Analyzed" reagent, was distilled from  $P_2O_5$ , and finally from  $CaH_2$  prior to use.<sup>47</sup> A mid-fraction from the final distillation was used both as solvent for the reaction studies and as solvent in the spectroscopic analysis. Carbon tetrachloride was of spectroscopic grade (Fluka). Benzene, diethyl ether, and various petroleum ethers were dried with sodium.

**Materials.** Lithium perchlorate (Fluka *purum*, wasserfrei) was dried for 2 h at  $10^{-3}$  mmHg prior to use.

Trityl chloride,  $Ph_3CCl$  (Fluka *purum*), was crystallized twice from petroleum ether, and finally from acetonitrile. The purified product was slightly yellow. Solutions of this compound for the experiment were made in the following way: Purified  $Ph_3CCl$  was allowed to dissolve in warm acetonitrile in a pre-weighed bottle. Upon cooling, most of the compound crystallized. The crystals were washed repeatedly with cold acetonitrile, and finally dried in vacuum to constant weight, in the bottle in which the dried product was later dissolved in acetonitrile and diluted to desired volume.

Trityl perchlorate,  $Ph_3CClO_4$ , was made according to Longworth and Mason,<sup>52</sup> from  $Ph_3CCl$  and excess anhydrous silver perchlorate (K & K Laboratories, Inc.). Solutions of the purified product were made in the same way as for  $Ph_3CCl$ .

Tetraphenylarsonium cyanide,  $Ph_4AsCN$ , was prepared from the corresponding chloride and potassium cyanide in methanol, according to Andreades and Zahnow,<sup>48</sup> or in water according to Norris.<sup>44</sup> The best yield was obtained with the former procedure. The product, after being dried in vacuum, was repeatedly dissolved in acetonitrile, some benzene added, and the solvent mixture evaporated in vacuum in order to remove traces of water to ensure a complete removal of potassium salts prior to the final crystallization from acetonitrile. Finally, the product was powdered in a mortar and dried to constant weight at  $10^{-3}$  mmHg in a pre-weighed bottle, in which the dried compound was later dissolved in acetonitrile and diluted to appropriate volume. Under no part of this salt's synthesis and purification, the temperature was allowed to rise above  $50^\circ C$ .

Extreme care was exercised to exclude moisture during the preparation of the above-mentioned reagents and their solutions.

Trityl cyanide,  $Ph_3CCN$ , was made from purified  $Ph_3CCl$  and cuprous cyanide, according to Budde and Potempa.<sup>47</sup> The product, crystallized from isopropyl alcohol and finally from cyclohexane, had m.p.  $128^\circ C$ .

Trityl isonitrile,  $Ph_3CNC$ , was made from  $Ph_3CCl$  and tetramethylammonium dicyanoargentate:<sup>12</sup> to 5.56 g  $Ph_3CCl$  dissolved in 250 ml acetonitrile was added 5.84 g tetramethylammonium dicyanoargentate under constant stirring, at room temperature. A white solid, presumably tetramethylammonium dichloroargentate, quickly precipitated. The reaction mixture was stirred for 90 min, whereupon the solvent was removed in vacuum and the product extracted from the residue with ether. After evaporation of the ether, 5.2 g (97 %, m.p.  $135^\circ C$ ) of the desired product was left in the bottle. Crystallized from petroleum ether ( $80-100^\circ C$ ), and finally from cyclohexane, the product had m.p.  $136^\circ C$ . (Found: C 89.31; H 5.56; N 4.98. Calc. for  $C_{20}H_{15}N$ : C 89.19; H 5.61; N 5.20.)

Trityl isonitrile dibromide,  $Ph_3CNCBr_2$ , was made by adding a solution of bromine in carbon tetrachloride to  $Ph_3CNC$  in the same solvent, until the reaction mixture turned slightly yellow-brownish. Upon cooling, the product precipitated as a white crystalline solid. A solution in carbon tetrachloride showed no absorbance in the  $2100-2300\text{ cm}^{-1}$  region, while a very strong new band at  $1698\text{ cm}^{-1}$ , due to  $C=N$ , could be detected. The crystalline product decomposed rapidly, changing its colour to yellow-greenish, and an

elemental analysis could thus not be performed. IR and m.p., 156°C, of the decomposition product showed it to be trityl bromide, the other product being presumably cyanogen bromide, as freshly prepared samples of  $\text{Ph}_3\text{CNCBr}_2$  had a pungent odour, similar to that of the latter. A solution of  $\text{Ph}_3\text{CNCBr}_2$  in acetonitrile turned yellow rapidly, while the compound appeared to be stable in carbon tetrachloride.

*Titration of  $\text{Ph}_3\text{CNC}$  with bromine in carbon tetrachloride.* On further study of the reaction between  $\text{Ph}_3\text{CNC}$  and bromine in carbon tetrachloride it was realized that titration of  $\text{Ph}_3\text{CNC}$  with bromine had a sharp visual end-point, and could be used as a quantitative method for the determination of  $\text{Ph}_3\text{CNC}$ . By performing the titration around 0°C, the end-point was even sharper: 0.6536 g  $\text{Ph}_3\text{CNC}$  was dissolved in 50 ml carbon tetrachloride, and cooled to 0°C. The solution was then titrated with a cold solution of 1.1075 g bromine in 25 ml carbon tetrachloride, until the first trace of yellow colour appeared. Found: 8.62 ml; calc. 8.80 ml. Several titrations were performed on both  $\text{Ph}_3\text{CNC}$  and benzhydryl isonitrile,<sup>12</sup> and usually 2 % less isonitrile was found than calculated. The presence of large excess of the corresponding cyanides,  $\text{Ph}_3\text{CCN}$  and diphenylacetoneitrile, was not found to interfere. Small amounts, however, of the corresponding alcohols,  $\text{Ph}_3\text{COH}$  and benzhydrol, made the end-point of the titrations diffuse.

*Products from  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_4\text{AsCN}$  in acetonitrile at 25°C.* Thermostated solutions of the two reagents, shielded from atmospheric moisture, were added together with stirring. The cyanide was always a few per cent in excess, to avoid the presence of unreacted  $\text{Ph}_3\text{CCl}$  during the work-up. As a linear correlation was found between the concentration of  $\text{Ph}_3\text{CNC}$  and the peak height at 2126  $\text{cm}^{-1}$  in acetonitrile, the yield of  $\text{Ph}_3\text{CNC}$  could be determined directly, if necessary after dilution, using an IR liquid cell with 0.1 cm path length.

As  $\text{Ph}_3\text{CCN}$  could not be determined quantitatively by IR in acetonitrile, the reaction mixture was evaporated to dryness in vacuum, and the residue was extracted repeatedly with ether. The total amount of  $\text{Ph}_3\text{CNC}$  and  $\text{Ph}_3\text{CCN}$  was then determined by weight after evaporation of the combined ether extracts. The total was close to 100 %, calculated from the amount of  $\text{Ph}_3\text{CCl}$  used. The mixture of  $\text{Ph}_3\text{CCN}$  and  $\text{Ph}_3\text{CNC}$  was dissolved in carbon tetrachloride, diluted to desired volume, and each of the products determined quantitatively, using an IR liquid cell. As the relative abundance of the two products was approximately the inverse of their extinction coefficients, two well separated peaks at 2126  $\text{cm}^{-1}$  and 2239  $\text{cm}^{-1}$  of rather similar intensities were obtained. The yields of each of the products were thus determined with rather like accuracy. The total amount of the products determined spectroscopically amounted to  $97 \pm 3$  % based on  $\text{Ph}_3\text{CCl}$ . Finally, the carbon tetrachloride solution of the products was titrated with bromine for an additional determination of  $\text{Ph}_3\text{CNC}$ .

From several experiments with reagents and acetonitrile from different batches, the yield of  $\text{Ph}_3\text{CNC}$ , determined by the three different procedures, was found to be  $9.5 \pm 1$  % at 25°C. The yield of  $\text{Ph}_3\text{CCN}$  was found to be  $89 \pm 4$  %. The product ratio was found not to be dependent upon the concentration of the reagents in the  $2 \times 10^{-2}$  –  $2 \times 10^{-1}$  M region.

Similar experiments with  $\text{Ph}_3\text{CClO}_4$  at 25°C gave, within the experimental error, the same product ratio of  $\text{Ph}_3\text{CCN}$  and  $\text{Ph}_3\text{CNC}$  as did  $\text{Ph}_3\text{CCl}$ .

Several unsuccessful attempts were made to separate the two isomeric products by crystallization. Attempts to reduce  $\text{Ph}_3\text{CNC}$  with lithium aluminium hydride failed.  $\text{Ph}_3\text{CCN}$  is known not to be reduced by this reagent.<sup>13</sup>  $\text{Ph}_3\text{CNC}$  was found not to yield the formamide or the Passerini product with hydrochloric acid in water and acetone, respectively.<sup>14</sup> Instead, a high yield of  $\text{Ph}_3\text{COH}$  was obtained.

*Reaction between  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_4\text{AsCN}$  at 25°C in acetonitrile in the presence of  $\text{LiClO}_4$ .* To a thermostated mixture of 2 ml 0.1476 M  $\text{Ph}_4\text{AsCN}$  and 2 ml 0.151 M  $\text{LiClO}_4$  was added 2 ml 0.1337 M  $\text{Ph}_3\text{CCl}$ . IR of the reaction mixture in acetonitrile showed no absorption at 2126  $\text{cm}^{-1}$ . In the carbon tetrachloride solution of the reaction mixture, a 100 % yield of  $\text{Ph}_3\text{CCN}$  was calculated from the peak-height at 2239  $\text{cm}^{-1}$ .

*Reaction between  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_4\text{AsCN}$  in acetonitrile at -17°C.* 10 ml 0.1476 M  $\text{Ph}_4\text{AsCN}$  and 10 ml 0.1337 M  $\text{Ph}_3\text{CCl}$  were cooled to -17°C and mixed at this temperature. The reaction mixture was kept at -17°C and then allowed to attain room temperature, and was analyzed in the usual way. Yield of  $\text{Ph}_3\text{CNC}$  and  $\text{Ph}_3\text{CCN}$ , 6 and 92 %, respectively.



*Reaction between  $\text{Ph}_3\text{CCl}$  and  $\text{Ph}_4\text{AsCN}$  in acetonitrile at  $81.5^\circ\text{C}$ .* The solution of  $\text{Ph}_4\text{AsCN}$ , 10 ml 0.1476 M, was added quickly to a refluxing solution of  $\text{Ph}_3\text{CCl}$ , 100 ml 0.01337 M. Immediately after the addition was over, the reaction mixture was cooled down, by external cooling, and by applying vacuum. Analysis at  $25^\circ\text{C}$  showed 17 %  $\text{Ph}_3\text{CNC}$ .

Separate experiments showed  $\text{Ph}_3\text{CNC}$  to isomerize rather rapidly in pure acetonitrile at  $25^\circ\text{C}$ , with a half-life of 2 h.<sup>60</sup> In the presence of  $\text{Ph}_4\text{AsCl}$ , however, as is the case in the experiments described here, the isomerization is very slow.

*Kinetic study of the reaction between  $\text{Ph}_4\text{AsCN}$  and methyl iodide in acetonitrile at  $25^\circ\text{C}$ .* The starting concentration of each of the reactants, after mixing, was  $1.00 \times 10^{-3}$  M. The reaction was studied spectrophotometrically at 247.5 m $\mu$ , using a Beckman DB Spectrophotometer. The extinction coefficient of the iodide ion at 247.5 m $\mu$  was determined with potassium iodide and with tetraphenylarsonium iodide. From the absorption of the latter was subtracted the absorption due to the tetraphenylarsonium ion, determined separately with tetraphenylarsonium dicyanoargentate.<sup>13</sup> The separate determinations of the extinction coefficient of the iodide ion,  $1.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , agreed within 1 %.

Values of the rate constant ranged from 25.5 to 27.7  $\text{M}^{-1} \text{ sec}^{-1}$ . No trace of methyl isonitrile could be detected in the products.

*IR instruments.* The quantitative determination of  $\text{Ph}_3\text{CNC}$  and  $\text{Ph}_3\text{CCN}$  was performed with a Unicam SP 200G Infrared Spectrophotometer. The integrated extinction coefficients of  $\text{Ph}_3\text{CNC}$  and  $\text{Ph}_3\text{CCN}$  in carbon tetrachloride were calculated from measurements performed with a Perkin Elmer 225 Grating Infrared Spectrophotometer.

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## REFERENCES

1. Kornblum, N., Smiley, R. A., Blackwood, R. A. and Iffland, D. C. *J. Am. Chem. Soc.* **77** (1955) 6269.
2. Hünig, S. *Angew. Chem. Intern. Ed.* **3** (1964) 548.
3. Pearson, R. G. and Songstad, J. J. *Am. Chem. Soc.* **89** (1967) 1827.
4. Gompper, R. *Angew. Chem. Intern. Ed.* **3** (1964) 560.
5. Norbury, A. H. and Sinha, A. I. P. *Quart. Rev. (London)* **24** (1970) 69.
6. Burmeister, J. L. *Coord. Rev.* **1** (1966) 205.
7. Burmeister, J. L. *Coord. Rev.* **3** (1968) 225.
8. Nef, J. U. *Ann.* **309** (1899) 154.
9. Davis, T. L. and Yelland, W. E. *J. Am. Chem. Soc.* **59** (1937) 1998.
10. Kurtz, P. In *Houben-Weyl*, Thieme, Stuttgart 1952, Vol. 8, p. 290.
11. Shriver, D. F. and Posner, J. J. *Am. Chem. Soc.* **88** (1966) 1672.
12. Songstad, J., Stangeland, L. J. and Austad, T. *Acta Chem. Scand.* **24** (1970) 355.
13. Hartley, E. G. J. *J. Chem. Soc.* **109** (1916) 1296.
14. King, R. B. *Inorg. Chem.* **6** (1967) 25.
15. Högl, F., Meir-Mohar, T. and Viditz, F. *Monatsh.* **52** (1929) 73.
16. Griffith, W. P. *Quart. Rev. (London)* **16** (1962) 188.
17. Purcell, K. F. *J. Am. Chem. Soc.* **89** (1967) 6139.
18. Bither, T. A., Knoth, W. H., Lindsay, Jr., R. V. and Sharkey, W. H. *J. Am. Chem. Soc.* **80** (1958) 4151.
19. Dulmage, W. L. and Lipscomb, W. N. *Acta Cryst.* **4** (1951) 330.
20. Haim, A. and Wilmarth, W. K. *J. Am. Chem. Soc.* **83** (1961) 509.
21. Burmeister, J. L. and Sutherland, D. *Chem. Commun.* **1965** 175.
22. Otsuka, S., Mori, K. and Yamagami, K. *J. Org. Chem.* **31** (1966) 4170.
23. Shriver, D. F. *Struct. Bonding (Berlin)* **1** (1966) 32.
24. Marshall, B. W. and Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1967** 7119.
25. Pocker, Y. and Parker, A. J. *J. Org. Chem.* **31** (1966) 1526.
26. Martin, D. and Weise, A. *Chem. Ber.* **99** (1966) 976.
27. Kuroda, K. and Gentile, P. S. *Inorg. Nucl. Chem. Letters* **3** (1967) 151.
28. Konya, K., Mishikava, H. and Shibita, M. *Inorg. Chem.* **7** (1968) 1165.
29. Birk, J. P. and Espenson, J. H. *J. Am. Chem. Soc.* **90** (1968) 2266.
30. Wagner, E. L. *J. Chem. Phys.* **43** (1965) 2728.

31. Bonaccorsi, R., Petrongolo, C., Scrocco, E. and Tomasi, J. *Theor. Chim. Acta*. **15** (1969) 332.
32. Doggett, G. and McKendrich, A. *J. Chem. Soc. A* **1970** 825.
33. Britton, D. *Perspect. Struct. Chem.* **1** (1967) 109.
34. Nordberg, R., Albridge, R. G., Bergmark, T., Ericson, U., Hedman, J., Nordling, C., Siegbahn, K. and Lindberg, B. *J. Arkiv Kemi* **28** (1968) 257.
35. Hendrichson, D. N., Hollander, J. M. and Jolly, W. L. *Inorg. Chem.* **8** (1969) 2642.
36. Booth, M. R. and Frankriss, S. G. *Spectrochim. Acta A* **26** (1970) 859.
37. Maloney, K. M. and Rabinovich, B. S. *J. Phys. Chem.* **73** (1969) 1652.
38. Pearson, R. G. *Survey Progr. Chem.* **5** (1969) 1.
39. Fava, A., Iliceto, A., Bresadola, S. *J. Am. Chem. Soc.* **87** (1965) 1405.
40. Tonellato, U. and Levorato, G. *Boll. Sci. Fac. Chim. Ind. Bologna* **27** (1969) 261.
41. Boughton, J. H. and Keller, R. N. *J. Inorg. Nucl. Chem.* **28** (1966) 2851.
42. Ritchie, C. D., Skinner, G. A. and Badding, V. G. *J. Am. Chem. Soc.* **89** (1967) 2063.
43. Parker, A. *J. Chem. Rev.* **69** (1969) 1.
44. Norris, A. R. *Can. J. Chem.* **47** (1969) 2895, 4267.
45. Andreades, S. and Zahnnow, E. W. *J. Am. Chem. Soc.* **91** (1969) 4181.
46. Walton, R. A. *Quart. Rev. (London)* **19** (1965) 126.
47. Coetzee, J. F. *Pure Appl. Chem.* **1967** 429.
48. Gutman, V. *Coordination Chemistry in Non-Aqueous Solvents*, Springer, Vienna 1968.
49. Pocker, Y. *J. Chem. Soc.* **1958** 240.
50. Pearson, R. G., Sobel, H. and Songstad, J. *J. Am. Chem. Soc.* **90** (1968) 319.
51. Baaz, M., Gutman, V. and Kruze, O. *Monatsh.* **93** (1962) 1142.
52. Longworth, W. R. and Mason, C. P. *J. Chem. Soc. A* **1966** 1164.
53. Hammond, G. S. *J. Am. Chem. Soc.* **77** (1955) 334.
54. Bijvoet, J. M. and Lely, J. A. *Rec Trav Chim.* **59** (1940) 908.
55. Lely, J. A. and Bijvoet, J. M. *Rec. Trav. Chim.* **61** (1942) 244.
56. Bak, B. *Dansk Kemi* **50** (1969) 121.
57. Johns, I. B. and DiPietro, H. R. *J. Org. Chem.* **29** (1964) 1970.
58. Ladd, M. F. C. *Trans. Faraday Soc.* **65** (1969) 2712.
59. Songstad, J. and Stangeland, L. *J. Acta Chem. Scand.* **24** (1970) 804.
60. Kerber, R. C. and Porter, A. *J. Am. Chem. Soc.* **91** (1969) 366.
61. Kornblum, N., Seltzer, R. and Haberfield, P. *J. Am. Chem. Soc.* **85** (1963) 1148.
62. Kurz, A. L., Beletskaya, I. P., Macias, A. and Reutov, O. A. *Tetrahedron Letters* **1968** 3679.
63. *National Bureau of Standards, Circular 500*, Washington DC 1952.
64. Schwarzenbach, G. and Schellenberg, M. *Helv. Chim. Acta* **48** (1965) 28.
65. Ahrland, S. *Helv. Chim. Acta* **50** (1967) 306.
66. Butler, R. N. and Symons, M. C. R. *Trans. Faraday Soc.* **65** (1969) 2559.
67. Budde, W. M. and Potempa, S. P. *J. Am. Chem. Soc.* **74** (1952) 258.
68. Nystrom, R. F. and Brown, W. G. *J. Am. Chem. Soc.* **70** (1948) 3738.
69. Austad, T. and Songstad, J. *To be published*.

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