°C under argon. When hydrogen evolution ceased, 3 (0.01 mol) in 50 mL of dioxane was added dropwise in 2 h. The reaction was continued for 8 h, cooled, and filtered. An oil, concentrated in 1, was eluted with toluene from a flash alumina (neutral) column and then further purified by distillation.

^{1}H NMR (δ) of 1. 1a: 1.16 (s, 12 H), 2.5 (br s, 1 H), 3.22 (s, 4 H), 3.5–3.7 (m, 12 H). **1b:** 1.16 (s, 12 H), 2.2 (br s, 1 H), 3.21 (s, 4 H), 3.5–3.8 (m, 16 H). **1c:** 0.85 (t, 3 H), 1.11 (s, 3 H), 1.14 (s, 3 H), 1.18 (s, 3 H), 1.2–1.5 (AB m, 2 H), 2.3 (br s, 1 H), 3.23 (s, 2 H), 3.27 (AB q, 2 H), 3.3–3.9 (m, 12 H). **1d:** 1.0–2.1 (m, 10 H), 1.17 (s, 6 H), 2.2 (br s, 1 H), 3.27 (s, 2 H), 3.42 (s, 2 H), 3.5–3.7 (m, 12 H). **1e:** 1.15 (s, 12 H), 2.8 (br s, 1 H), 3.25 (s, 4 H), 3.4–3.8 (m, 8 H).

Nitroxyl Radicals of 1.[9] To a solution of 1 (3 mmol) in 5 mL of methanol were added 0.35 mL of acetonitrile, 0.18 g of sodium bicarbonate, and 0.03 g of sodium tungstate. While stirring, 1 mL of 30% hydrogen peroxide was added in 5 min. The reaction was stirred under argon for 2 days. Saturated sodium chloride solution (20 mL) was added and the pH was adjusted to ~4 with 1 N HCl (~3 mL was needed). This aqueous solution was extracted with 3 × 50 mL of ether. The combined etherate solution was dried over magnesium sulfate and concentrated under vacuum. The wine-colored oil was pure in field-desorption mass spectrum.

Registry No. 1a, 93565-31-2; **1a** nitroxyl radical, 93565-35-6; **1a**–Li, 93565-37-8; **1b**, 93565-32-3; **1b** nitroxyl radical, 93565-36-7; **1c**, 93604-19-4; **1d**, 93565-33-4; **1e**, 93565-34-5; **2a**, 44982-72-1; **2c**, 90017-23-5; **2d**, 90017-24-6; **3a**, 19249-03-7; **3b**, 37860-51-8; **3e**, 7460-82-4; Na, 7440-23-5; K, 7440-09-7; Li, 7439-93-2; $(CH_3)_2CHC(O)OEt$, 97-62-1; $PhC(O)C(CH_3)_2C(O)OEt$, 25491-42-3; PhC(O)Cl, 98-88-4.

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Supported Cyanides: The Interaction of Potassium Cyanide with High Surface Area Inorganic Support Materials and the Development of Highly Reactive Cyanide Reagents

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Supported reagents formed by the adsorption of reagent molecules or ions onto the surface of inorganic solid supports have been successfully applied to a wide variety of organic reactions and have been shown to have many advantages over the pure reagents including increased selectivity, reactivity, and stereospecificity as well as manipulative convenience.[1,2] The subject was reviewed by McKillop in 1979[1] and a large number of articles have appeared in the literature since then. While supported reagents have been applied to many of the most important organic reaction types, little progress has been made with studies on the supported reagents themselves although significant improvements in reagent reactivity can be gained from such studies.[3,4] We have used infrared spectroscopy and X-ray diffraction to study one particular group of these materials, supported cyanides, which are known to be useful[5–7] but sometimes troublesome[7] sources of the cyanide ion in nucleophilic displacement reactions. Our analytical studies have enabled us to produce reagents that are significantly more reactive and more selective than previous materials.

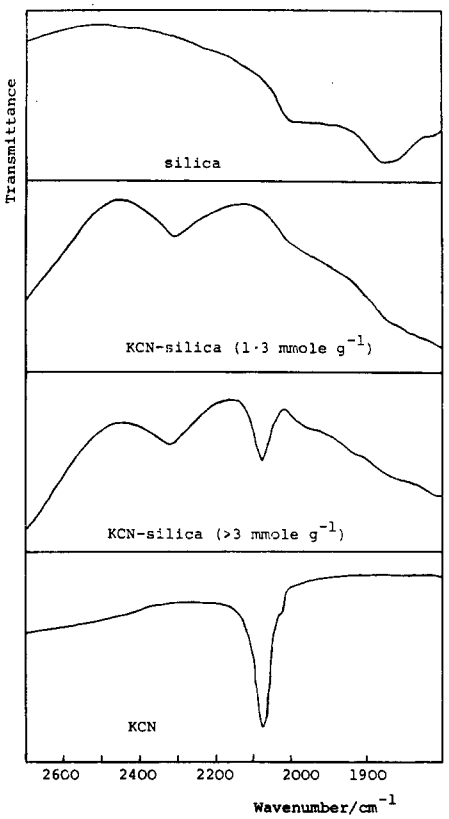

Figure 1. Infrared spectra of KCN–silica and its parents.

Results and Discussion

There are many high surface area inorganic materials that can be used as supports for preparing supported reagents. The two most popular support materials are silica gel and alumina and we have chosen these materials for our investigations. Many different commercial forms of these materials are available and this can lead to considerable confusion among workers attempting to reproduce literature recipes. We have consistently used three support materials, a Merck silica gel (surface area 400 m^2 g^{-1}, average pore diameter 100 Å), a BDH neutral alumina (surface area ca. 100 m^2 g^{-1}, average pore diameter 40 Å), and a partially fluorinated BDH alumina. The last of these materials was used so as to investigate the effects of enhanced surface acidity[8] on the reactivity of the resulting KCN–"F-alumina" reagent. Potassium cyanide was used throughout the study.

Potassium cyanide can be easily adsorbed onto supports by slow evaporation of a well-agitated mixture of the support and aqueous KCN. The resulting solid reagents are free flowing powders only if the KCN loading is below 5 molecules/nm^2 (this corresponds to at least one surface hydroxyl/KCN). Analysis of such free flowing powders enables us to distinguish between chemisorbed and physisorbed cyanide and to optimize dispersion of KCN on the surface of the support.

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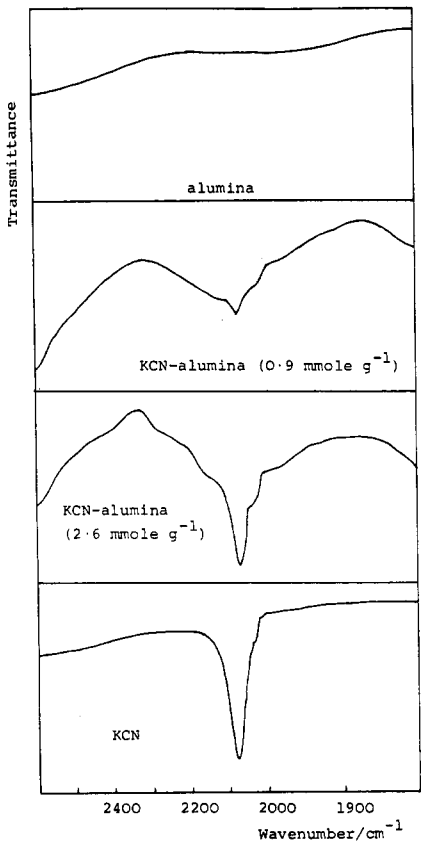

Figure 2. Infrared spectra of KCN–alumina and its parents.

The infrared spectra in the 2500–2000-cm^{-1} region of KCN–silica and KCN–alumina prepared at different loadings of KCN are shown in Figures 1 and 2, respectively, along with the spectra of the parent species. The infrared spectrum in this region of KCN–F-alumina is very similar to that of KCN–alumina although the cyanide band is somewhat broader in the latter. The most striking change observed in Figure 1 is the large shift in the ν(C≡N) band from 2076 cm^{-1} in KCN to 2300 cm^{-1} in KCN–silica. We believe that such a shift can only be a result of a chemisorption process resulting in the formation of Si–CN groups on the surface of the silica. A shift of 200 cm^{-1} cannot be attributable to hydrogen bonding or other weak interaction with the surface but the observed position of the cyanide band in KCN–silica is not unreasonable for a $(-O)_3$ SiCN species. To further support this conclusion, we have found that KCN cannot be removed from KCN–silica reagents with cyanide loadings of less than 5 molecules/nm^2.

In contrast to the KCN–silica reagent, KCN–alumina gave a broadened but only slightly shifted ν(C≡N) band. The breadth of this band is probably a result of there being several different cyanide orientations on the support surface (including those with the carbon, nitrogen, and triple bond directed toward the surface hydroxyl groups). Different degrees of ion–ion interactions may also occur on the support surface. The presence of excess cyanide (present as nondispersed microcrystals) is clearly evident in the infrared spectra at KCN loadings greater than 5 molecules/nm^2. It is interesting to note that when deliberately large amounts of KCN were used in the reagent preparation (i.e., >5 molecules/nm^2), the resulting non-free-flowing powder gave an infrared spectrum dominated by the free cyanide band at 2076 cm^{-1} whereas the free-flowing powder simultaneously produced in the evaporation showed only a small amount of free cyanide to be present. We were able to quantitatively remove the KCN from all of the KCN–alumina and KCN–F-alumina reagents confirming the physisorbed nature of the cyanide.

We have also found that X-ray diffraction can be used to identify excess, nondispersed cyanide although the method is less sensitive than infrared spectroscopy so that at a loading of 1 mmol of KCN/g of support, for example, we were unable to identify excess KCN at levels below 4% of the salt (0.2% of the total weight). Reagents that showed significant excess cyanide by infrared spectroscopy also showed a series of X-ray lines corresponding to those of the support and to those of KCN. Reagents that did not show infrared activity attributable to excess cyanide gave lines due to the support only. These observations are consistent with the efficient dispersion of KCN onto the support surface at loadings of less than 5 molecules/nm^2. At higher KCN loadings, clusters of ions must begin to form creating KCN microcrystals.

A major factor in determining the increase in reaction rate brought about by use of an inorganic support material in the reaction system must be the effective increase in reagent surface area due to adsorption of the reagent onto the support surface. Even a well-ground salt is unlikely to have a surface area of greater than 10 m^2/g so that efficient dispersion of that salt onto a support material of surface area 100 m^2/g, for example, should result in a significant improvement in salt reactivity in heterogeneous reaction systems. Both presupported salt reagents and salt–support mixtures have been employed in synthesis but we believe that efficient predispersion of the salt onto the support surface can only improve reagent reactivity and efficiency as long as the adsorption process does not result in a significant loss in salt reactivity due to charge redistribution. Loss in reagent efficiency can also result from the trapping of reactant ions within micropores inaccessible to substrate molecules. The analytical evidence derived thus far suggests that of the reagents investigated KCN–alumina and KCN–F-alumina with KCN loadings of about 5 molecules/nm^2 (0.9 mmol of KCN/g) should provide optimum reactivity and efficiency. This conclusion has been borne out by our reaction studies.

The reaction of 2.5 mol equiv of our optimized KCN–alumina and KCN–F-alumina reagents with benzyl chloride in a variety of solvents gave rapid and quantitative conversion of the substrate to benzyl cyanide. The rate of this reaction was approximately solvent independent suggesting that reaction occurs at the support surface rather than with free cyanide in solution (Figure 3). The only significant "solvent effect" is observed in the recovery of the product so that use of the very low polarity petroleum ether required more extensive washing of the reacted reagent if good recovered yields were to be obtained. The observed rates of reaction are appreciably greater than those observed previously using nonoptimized reagents[7] and thus justify the preliminary analytical studies. It is also interesting to note that unlike previous reports, our mechanically agitated reaction systems did not give any products resulting from Friedel–Crafts products in reactions employing toluene as solvent.[7] We suggest that the acid sites on the surface of the alumina support (and even on the surface of the more acidic F-alumina) which are responsible for catalyzing Friedel–Crafts reaction are effectively blocked by the dispersed cyanide. No reaction was observed in systems employing KCN–silica, consistent with the presence of a chemically bonded and inert CN group.

The method of converting benzyl chlorides to their respective cyanides using our optimized reagents is quite

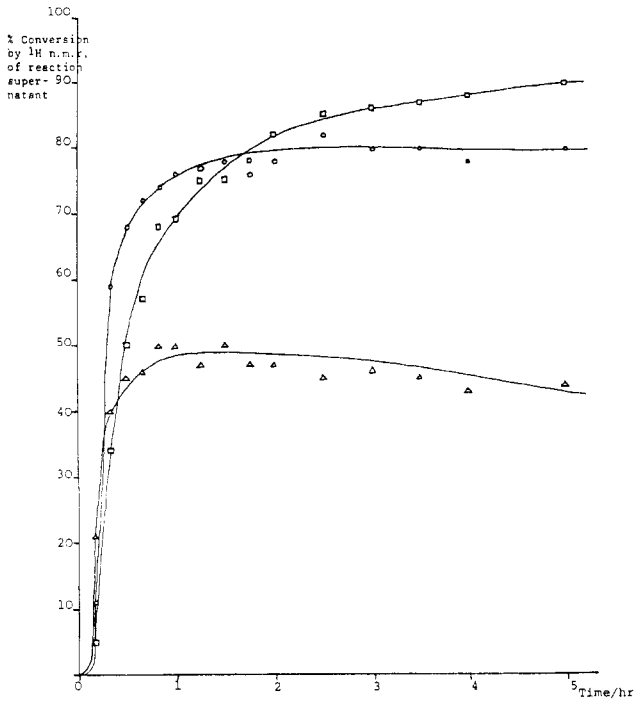

Figure 3. Rate of formation of benzyl cyanide from the reaction of benzyl chloride with 2.5 mol equiv of optimized KCN–F-alumina in (□) acetonitrile, (○) toluene, and (△) petroleum ether (80–100) at ca. 80 °C. Recovered yields may be greater than observed here (see text).

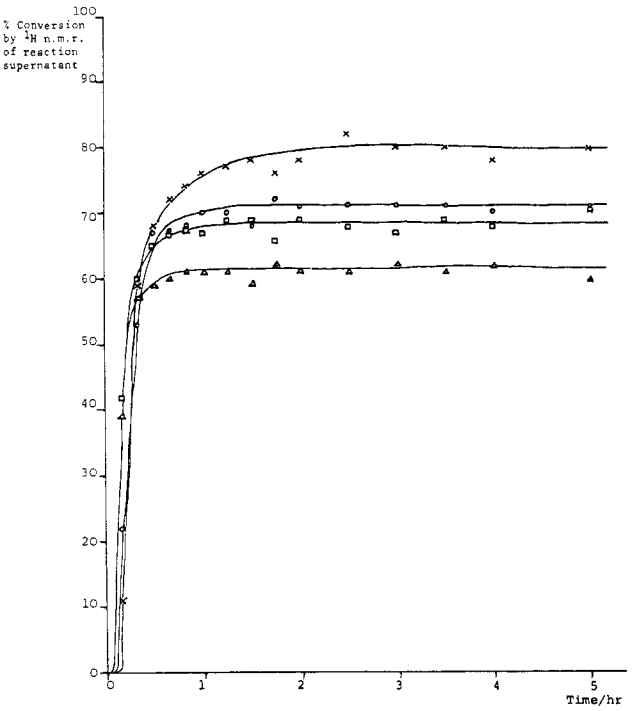

Figure 4. Rate of formation of benzyl cyanides from the reaction of the respective chlorides with 2.5 mol equiv of optimized KCN–F-alumina in refluxing toluene: (×) C_6H_5Cl, (○) *o*-$CH_3C_6H_4Cl$, (□) *p*-$CH_3C_6H_4Cl$; (△) *p*-*t*-BuC_6H_4Cl.

general. The rate curves for reactions of several substituted benzyl chlorides are shown in Figure 4. Reaction rates were generally similar in reactions employing the optimized KCN–alumina and KCN–F-alumina although the products were sometimes rather more easy to recover from systems involving the latter reagent. This suggests that while the enhanced acidity of the partially fluorinated surface of F-alumina has little effect on the reactivity of the reagent, the reduction in surface hydroxyls may act to reduce product–support interactions.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer 683 ratio recording spectrophotometer interfaced to a 64K dedicated computer for spectral processing. Spectra were usually obtained from a disc made up of KBr and reagent in the ratio 20:1 by weight. Spectra were found to be independent of the type of window material. X-Ray photographs were obtained with a Debye-Scherrer Chamber 807 camera. Powdered samples were mounted on a glass filament using glue. Exposure times were typically about 6 h.

The silica and alumina supports were provided by BDH (see text). F-Alumina was prepared at the University of Leicester by treatment of the alumina with elemental fluorine at a final F_2 pressure of 400 mmHg. Solvents were routinely dried before use but all other chemicals were commercial materials used without further treatment. The supported reagents were prepared by thorough mixing of a solution of KCN in water (usually 1 M) with the required amount of the support followed by slow evaporation of the mixture on a rotary evaporator. Final drying of the resulting white solids is achieved at 100 °C and <1 mmHg for not less than 12 h. The final materials should be free flowing powders (at or near optimum loadings).

Reactions were carried out in ordinary glassware with use of a mechanical stirrer to ensure good agitation. The reactions were monitored by ^1H NMR and products were known materials identified by NMR, IR, and mass spectrometry. In a typical reaction, benzyl chloride (3.2 g, 0.025 mol) was added to a mixture of the supported cyanide (75 g of the optimized KCN–alumina, for example, which is equivalent to 0.0625 mol of KCN) and the solvent (ca. 2× the weight with respect to the weight of the reagent, e.g., 150 g.). The resulting mixture was then brought to reflux with stirring, and the supernatant monitored by ^1H NMR until no further increase in the amount of product was observed. The mixture was then filtered and the solid material washed with 150 cm^3 of diethyl ether. The combined solutions were evaporated to dryness, and the resulting product was analyzed. The purity of the products obtained in this way was better than 99% by NMR and typical recovered yields were better than 75% (higher yields could be obtained by more thorough washing of the solid residues).

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Registry No. KCN, 151-50-8; alumina, 1344-28-1; fluorine, 7782-41-4; benzyl chloride, 100-44-7; benzyl cyanide, 140-29-4.

Selective Oxidation of Alcohols by Oxoaminium Salts ($R_2N{=}O^+X^-$)

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1-Oxo-2,2,6,6-tetramethylpiperidinium salt (I)[1,2] is known as an oxidizing agent of alcohols to the corresponding carbonyl compounds.[3,4] A kinetic study of this

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