pathway progresses along a relatively flat potential energy surface without temperature-dependent steps.

Experimental Section[14]

Photoreaction. A 1×10^{-2} M solution of 1,5-dimethylpyrazole (1) in acetonitrile was placed in a quartz tube and sealed with a rubber septum. The solution was degassed by bubbling dry nitrogen through the sample for 5 min. Initial reactant concentrations were measured using gas chromatography.[2] The quartz reaction tube was placed into a quartz dewar such that nitrogen could be passed over the tube. In order to cool the reaction solution to the desired temperature, the nitrogen gas which was passed over the reaction tube was initially passed through coils immersed in liquid nitrogen. The temperature was controlled by adjusting the flow rate of nitrogen through the coils and over the sample tube. The reaction temperature was monitored using an Omega 2175A digital thermocouple in which the thermocouple was passed through the rubber septum into the reaction solution. Irradiation was carried out using a 450-Watt high pressure mercury lamp.

Conclusion

Results indicate a dramatic temperature dependence for the formation of 1,2-dimethylimidazole (2) and 1,4-dimethylimidazole (3) in the phototransposition of 1,5-dimethylpyrazole (1) and in the phototransposition of 2 to 3. As the reaction temperature decreases, the amount of 3 decreases and the amount of 2 increases. This is strong evidence for a ground-state thermal reaction, which supports theoretical calculations using the MNDO Hamiltonian. Furthermore, these results support the proposed nitrogen walk mechanism for the formation of the imidazoles formed by the P_6 and P_7 pathways. The fact that the P_6 product 2 is produced at the expense of the P_7 product 3 suggests that the 2,5-diazabicyclo[2.1.0]pentene precursor to 2 via the P_6 pathway is also the precursor to 3 on the P_7 pathway and that the barrier to rearomatization of I_2 to 2 is smaller than the activation enthalpy for undergoing the second [1,3]-sigmatropic shift of nitrogen to provide I_3.

Registry No. 1, 694-31-5; 2, 1739-84-0; 3, 6338-45-0; 4, 10447-93-5.

(14) See ref 2 for the preparation of reactants and products and for a description of the general analytical procedures.

Regiospecific Reactions of the Ambident Anion of Bis(pentamethylphenyl)acetonitrile

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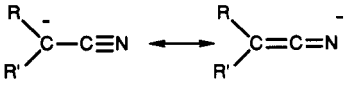
There are many examples in the literature that illustrate the regiospecificity of reaction with salts of acetonitrile derivatives.[1a-d] While the ambident anion 1 offers two potential sites for electrophilic attack (C or N as in **1a** and **1b**, respectively), C-alkylation almost invariably predominates.[1e-k]



1a **1b**

This preponderance of C- over N-alkylation of nitrile "carbanions" is not unlike the reaction between electrophiles and the conjugate bases of aldehydes, ketones, esters, and amides.[2] Here, however, the influence of temperature, solvent, and counterion on the ratio of C- to O-alkylation appears to be more pronounced.[3] The importance of these factors in the alkylation of nitriles can be seen in the clean C-monoalkylation of primary nitriles which can permit successive alkylations using different alkylating agents useful in the preparation of a specific nitrile derivative such as a carboxylic acid or amine.[4]

The regiospecificity of 1 with electrophiles suggests that carbon is more nucleophilic than nitrogen. This, however, is strongly influenced by steric hindrance both in the electrophile and nitrile moieties. The few examples[5,6] which illustrate this involve bulky alkyl groups; for example, the isopropylation of diisopropylacetonitrile in alkaline conditions affords triisopropylacetonitrile and *N*-isopropyldiisopropylketene imine in 70% and 23% yields, respectively. We now wish to report the effects of the novel bulky aryl group, pentamethylphenyl, C_6Me_5 (Scheme I), in directing the site of alkylation.

Bis(pentamethylphenyl)acetonitrile (2), which is among the most hindered diarylacetonitriles synthesized to date, requires highly basic conditions for its deprotonation to form 3. This lithium "carbanion" is air sensitive; exposure of the yellow solution to atmospheric oxygen results in a rapid change to dark purple due to the oxidation of 3 to the radical cyanobis(pentamethylphenyl)methyl (4) which has been isolated as a stable crimson colored solid.[7]

An IR spectrum of 3 taken in THF in the absence of oxygen showed strong absorptions at 2044 and 2080 cm^{-1} (shoulder). These heterocumulene values suggest that 3 exists as an *N*-lithio, **1b**, rather than a *C*-lithio, **1a**, salt. A direct comparison can be made with the monolithium salt of phenylacetonitrile [ν(C=C=N) 2065 cm^{-1}] whose dimeric structure in the solid state is believed to be retained in solution.[8]

The significant degree of steric hindrance provided by the pentamethyl groups was illustrated by the exclusive N-alkylation of 3 with methyl iodide. When bis(pentamethylphenyl)acetonitrile (2) was deprotonated with 3 molar equiv of *n*-BuLi·TMEDA the yield of *N*-methylbis(pentamethylphenyl)ketene imine (6) [ν(C=C=N) 2016 cm^{-1}] was ca. 80%. There was no evidence for a C-alkylated acetonitrile in the crude product. On using less than this optimum quantity of base, the isolated yield of 6 was significantly reduced (1 mol equiv of base gave 6 and unreacted 2 in 22% and 57% yields, respectively). The structure of the *N*-methylketene imine 6 was confirmed by its independent synthesis from *N*-methylbis(penta-

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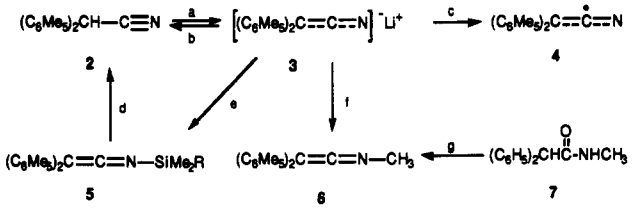
0022-3263/92/1957-1940$03.00/0

Scheme I[a]



[a] Key: (a) 3 equiv of *n*-BuLi–TMEDA; (b) CF_3CO_2H; (c) O_2 (air); (d) H^+/TBAF; (e) RMe_2SiCl; (f) CH_3I; (g) $Br_2/Ph_3P/Et_3N$.

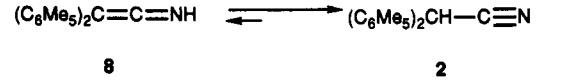
methylphenyl)acetamide (7). This was accomplished in 66% yield by the bromination/dehydrobromination of 7 using a mixture of bromine, triethylamine, and triphenylphosphine in refluxing dichloromethane.

Nitriles are generally silylated regioselectively in the α-position by reagents such as $Me_3SiOSO_2CF_3/Et_3N$ in Et_2O at 0–20 °C.[9,10] The mechanism for this reaction has been reported to involve silylation on the cyano nitrogen atom to form a nitrilium ion and deprotonation of this intermediate to yield an *N*-silylketene imine which then undergoes a 1,3-N to C rearrangement to yield the thermodynamically more stable C-silylated tautomer as the final product.

We have formed this intermediate in solution by trapping of the ambident anion 3 with trimethylsilyl chloride. An IR spectrum of the crude product confirmed the presence of *N*-(trimethylsilyl)bis(pentamethylphenyl)-ketene imine (5) (R = CH_3), ν(C=C=N) 2055 cm^{-1}, but on workup bis(pentamethylphenyl)acetonitrile (2) was isolated.

The behavior of the *N*-(trimethylsilyl)ketene imine 5 can be compared with trimethylsilyl enol ethers which are also susceptible to rapid solvolysis in protic media (either in the presence of acid or base) and therefore not broadly useful in synthesis.[11] The *tert*-butyldimethylsiloxy group, however, is ca. 10^4 times more stable than trimethylsiloxy;[12] accordingly, the lithium salt of bis(pentamethylphenyl)-ketene imine (3) was treated with *tert*-butyldimethylsilyl chloride. The product obtained was *N*-(*tert*-butyldimethylsilyl)bis(pentamethylphenyl)ketene imine (5) (R = *t*-Bu), ν(C=C=N) 2068 cm^{-1}, isolated as a bright yellow solid although it requires careful handling during workup due to its desilylation by residual TMEDA. The complete regiospecificity of the silylation reaction was shown by a lack of extra peaks in the ^{1}H-NMR and IR spectra of the crude product.

Only in the case of steric hindrance in the α-position and/or extended conjugation can the isomer of *N*-silylketene imine attain comparable thermodynamic stability and be isolated.[10] The trimethylsilylation of acetonitrile, for example, yields (trimethylsilyl)acetonitrile and *N*-(trimethylsilyl)bis(trimethylsilyl)ketene imine in yields of 56% and 44%, respectively.[9,13] The nature of the silylating agent is also important. For example, the silylation of the α-cyano "carbanion" 1 (R = Ar, R^1 = Me, Et, *i*-Pr) with *tert*-butyldimethylsilyl chloride affords an *N*-silylketene imine in high yield while trimethylsilyl chloride predominantly gives the C-silylated product Ar(R)C(SiMe$_3$)CN.[14,15]



In line with the synthesis of the *N*-alkyl- and *N*-silylketene imines 6 and 5, respectively, we have also investigated the possibility of generating the N–H ketene imine 8; the less stable tautomeric form of bis(pentamethylphenyl)acetonitrile (2). The protonation of 3 on a preparative scale with 1 mol equiv of trifluoroacetic acid in tetrahydrofuran gave on workup the C–H compound 2 in high yield. The desilylation of *N*-(*tert*-butyldimethylsilyl)bis(pentamethylphenyl)ketene imine (5) (R = *t*-Bu) with tetrabutylammonium fluoride in THF, on the other hand, shows three absorptions in the IR spectrum of the reaction mixture; 2230 cm^{-1} which corresponded to the diarylacetonitrile 2, 2063 cm^{-1} which was confirmed as the *N*-silylketene imine 5 (R = *t*-Bu), and finally an intense absorption at 2147 cm^{-1}. This was unlikely to be due to cyanobis(pentamethylphenyl)methyl (4) (ν(C=C=N) 2116 cm^{-1}) because neither the reaction mixture nor the spectroscopic sample displayed the vivid red/purple color of the radical (although this color did develop after 10–15 h on standing). Addition of acid caused the absorption at 2147 cm^{-1} to disappear. These results are consistent with this absorption corresponding to bis(pentamethylphenyl)ketene imine (8). While this novel N-unsubstituted ketene imine appeared to be stable for several hours in dilute solution, it undergoes acid-catalyzed prototropic rearrangement to its thermodynamically more stable acetonitrile tautomer 2. The oxidation of 8 to the radical 4 is not unlike the facile conversions of enols to α-acylmethyl radicals.[16,17]

While the hydrolysis of *N*-(trimethylsilyl)benzophenone imines gives an N–H imine,[18,19] the alcoholysis of *N*-silylketene imines have only been reported to afford acetonitriles without the detection of an N–H ketene imine intermediate.[14] Such intermediates have been reported for ferrocenyl and dicyano ketenimines[9,20,21] with heterocumulene absorptions (2200–2185 cm^{-1}) in agreement with that for 8, but the steric properties of the C_6Me_5 group appears to make the latter system a good candidate for further studies of ketene imine/nitrile tautomerism.

Experimental Section

IR and ^{1}H-NMR spectra were recorded at 60 and 270 MHz. Melting point values are uncorrected. Silica gel (Merck Art. 9385) was the medium used for flash chromatography (4 × 17 cm; medium pressure). Commercial reagents were used without further purification unless otherwise stated.

Bis(pentamethylphenyl)acetic Acid. Pentamethylbenzene (101.65 g, 0.68 mol) and glyoxylic acid hydrate (22.38 g, 0.25 mol) were dissolved in warm acetic acid (323 mL) and cooled in an ice bath, and concentrated sulfuric acid (198 mL) was added over 0.75 h. The resulting thick red suspension was stirred at ambient temperature for 2 d and was then poured into water (1 L), and the product was extracted with ether (1 L). After washing with saturated aqueous NaCl and drying with anhydrous $MgSO_4$, the organic solution was evaporated to dryness. The crude product was recrystallized from 1-propanol to afford bis(pentamethylphenyl)acetic acid (61.2 g, 71%), mp 254–256 °C: ^{1}H-NMR ($CDCl_3$) δ 2.07 (s, 12 H), 2.18 (s, 12 H), 2.23 (s, 6 H), 5.60 (s, 1

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H), 10.95 (s, 1 H, exchangeable); IR (KBr) 3325 (OH), 2926 (CH), 1704 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_2$: C, 81.77; H, 9.15. Found: C, 82.30; H, 9.42.

Bis(pentamethylphenyl)ketene. Thionyl chloride (2 mL, 27.2 mmol) was added to a cold suspension of bis(pentamethylphenyl)acetic acid (8.0 g, 22.7 mmol) in dry toluene (80 mL). Pyridine (two drops) was added, and the mixture was refluxed for 1.5 h. The hot solution was then treated twice with charcoal and filtered. After rotary evaporation of the solvent the crude product was recrystallized from acetonitrile to yield bis(pentamethylphenyl)ketene (5.9 g, 78%) as bright yellow crystals of mp 153–156 °C: ^{1}H-NMR ($CDCl_3$) δ 2.15 (s, 12 H), 2.21 (s, 12 H), 2.25 (s, 6 H), IR (KBr) 2093 (C=C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04. Found: C, 86.28; H, 9.06.

***N*-Methylbis(pentamethylphenyl)acetamide.** Bis(pentamethylphenyl)ketene (5 g, 15 mmol) was dissolved in dry toluene (300 mL), and anhyd methylamine was bubbled through the vigorously stirred solution for 2.5 h. The reaction which ensued was mildly exothermic. The crude product which precipitated was then removed by filtration and recrystallized from methanol to afford *N*-methylbis(pentamethylphenyl)acetamide (5.25 g, 52%), mp 258–260 °C: ^{1}H-NMR ($CDCl_3$) δ 2.03 (s, 12 H), 2.17 (s, 12 H), 2.23 (s, 6 H), 2.80 (δ, 3 H, J = 4.95 Hz), 5.38 (s, 1 H), 5.73 (1 H); IR (KBr) 3378, 3310 (NH), 2915 (OH), 1647 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{35}NO$: C, 81.53; H, 9.98; N, 3.96. Found: C, 81.76; H, 9.98; N, 3.68.

***N*-Methylbis(pentamethylphenyl)ketene Imine. Method 1.** Bromine (0.2 mL, 3.9 mmol), triethylamine (2.74 mL, 19.7 mmol), and *N*-methylbis(pentamethylphenyl)acetamide (1.39 g, 3.9 mmol) were added in this order to triphenylphosphine (1.03 g, 3.9 mmol) dissolved in dry CH_2Cl_2 (50 mL). After the mixture was heated under reflux for 1 h, sufficient silica gel was added to the flask for the reaction mixture to cake. Removal of residual solvent on a rotary evaporator gave a powder which was then added to a pretreated (CCl_4) chromatographic column and eluted with CCl_4 under applied pressure. The elution was monitored by TLC (1:19 ether/petroleum ether (60–80 °C)), and the fraction with Rf 0.56 was evaporated to dryness to afford *N*-methylbis(pentamethylphenyl)ketene imine (0.90 g, 66%). This pale yellow solid was recrystallized from dry ether to give white needle-like crystals (0.63 g, 46%), mp 181–182 °C.

Method 2. Tetramethylenediamine (0.32 mL, 2.16 mmol) and *n*-BuLi (1.38 mL, 2.16 mmol) were added to a solution, at ambient temperature, of bis(pentamethylphenyl)acetonitrile (0.24 g, 0.72 mmol) in THF (3 mL) under an atmosphere of dry nitrogen. The reaction mixture was stirred for 30 min and then cooled to −78 °C before dimethyl sulfate (0.27 mL, 2.88 mmol) was added. After being stirred for 1 h at ambient temperature, the reaction mixture was poured into ether/water (1:1) and the combined ether extract was dried with anhydrous $MgSO_4$. ^{1}H-NMR analysis of the crude residue obtained on evaporation of the solvent indicated only the presence of *N*-methylbis(pentamethylphenyl)ketene imine. Purification by flash chromatography (1:19 ether/petroleum ether (60–80 °C)) afforded 0.21 g (81%) of product.

***N*-(*tert*-Butyldimethylsilyl)bis(pentamethylphenyl)ketene Imine.** Anhydrous *tert*-butyldimethylsilyl chloride (0.68 g, 4.5 mmol) in 4 mL of dry THF was added to a −78 °C solution of the lithium salt of bis(pentamethylphenyl)ketene imine prepared from bis(pentamethylphenyl)acetonitrile (0.5 g, 1.5 mmol), tetramethylenediamine (0.68 mL, 4.5 mmol), and *n*-BuLi (2.8 mL, 4.5 mmol) in dry THF (5 mL). The bright yellow reaction mixture was stirred for 1.5 h at room temperature before sufficient silica gel was added for it to cake. After residual solvent was removed on a rotary evaporator the remaining powder was flash chromatographed (1:19 ether/petroleum ether). The bright yellow band which eluted gave an oil which solidified on removing the solvent. Recrystallization from acetonitrile gave *N*-(*tert*-butyldimethylsilyl)bis(pentamethylphenyl)ketene imine, mp 160–164 °C: ^{1}H-NMR ($CDCl_3$) δ 0.22 (s, 6 H), 0.90 (s, 9 H), 2.09 (s, 12 H), 2.19 (s, 12 H), 2.23 (s, 6 H); IR (KBr) 2068 (C=C=N) cm^{-1}. Anal. Calcd for $C_{30}H_{45}NSi$: C, 80.47; H, 10.13; N, 3.13. Found: C, 80.10; H, 10.47; N, 2.86.

Similarly prepared was ***N*-(trimethylsilyl)bis(pentamethylphenyl)ketene Imine.** Purification of the off-white crude product was not possible due to facile hydrolysis to bis(pentamethylphenyl)acetonitrile. Storage under a dry inert atmosphere, however, retarded decomposition: IR (KBr) 2055 cm^{-1}.

Desilylation of *N*-(*tert*-Butyldimethylsilyl)bis(pentamethylphenyl)ketene Imine. Two equiv of tetrabutylammonium fluoride in THF (0.84 mL of a 1 M solution; 0.84 mol) was added to a deoxygenated solution of *N*-(*tert*-butyldimethylsilyl)bis(pentamethylphenyl)ketene imine (0.19 g, 0.42 mmol) in THF (5 mL). IR analysis (2000–2300 cm^{-1}) of the resulting yellow solution after 10 min revealed three absorptions of approximately equal intensity: 2230 cm^{-1} (bis(pentamethylphenyl)acetonitrile); 2147 cm^{-1} (tentatively assigned to N–H bis(pentamethylphenyl)ketene imine), and 2063 cm^{-1} (*N*-*tert*-butyldimethylsilyl)bis(pentamethylphenyl)ketene imine. A second spectrum taken after 17 h showed that the absorption at 2147 cm^{-1} had increased while the absorption at 2063 cm^{-1} had decreased. Addition of a drop of acetic acid to the reaction mixture resulted in the complete disappearance of the absorption at 2147 cm^{-1} with bis(pentamethylphenyl)acetonitrile being the only product.