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REACTION OF PYRIDINE N-IMIDES WITH YLIDENEMALONONITRILES: FORMATION OF A NOVEL INTRAMOLECULAR PYRIDINIUM SALT

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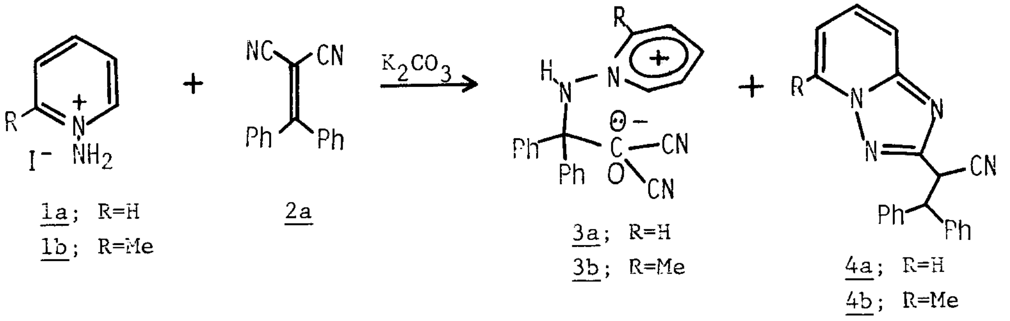
Abstract: Pyridine N-imides react with ylidenemalononitriles to form a novel intramolecular pyridinium salt containing a dipole structure.

During the course of our investigation concerning the pyridine N-imides chemistry, we have discovered recently that reaction of pyridine N-imides with tetra-substituted olefins leads to the formation of novel products,[2,3] since the usual 1,3-dipolar cycloaddition reaction followed by dehydrogenation to give pyrazolo[1,5-a]pyridine derivatives[4] is not allowed. In this connection we have investigated the reaction of pyridine N-imides with several tetra-substituted olefins and found that ylidenemalononitriles[5] undergo another interesting reaction with pyridine N-imides.

When a solution of 1-aminopyridinium iodide (1a) and (α-phenylbenzylidene)-malononitrile (2a) (1.2 : 1.0 equiv) was stirred at room temperature in the presence of potassium carbonate for 4h, two products 3a (mp 224-225 °C, 40 %) and 4a (mp 181-182 °C, 12 %) were isolated after separation by column chromatography on silica gel. The structures of 3a and 4a were determined mainly on the basis of the spectral data. The elemental analyses and mass spectra of 3a and 4a indicate that both of them are 1:1 adducts of pyridine N-imide and yledenemalononitrile 2a. The product 3a is a violet powdery solid and the dipole structure was suggested by its UV spectrum shown in Table 1 in which



1a; R=H
1b; R=Me

2a

3a; R=H
3b; R=Me

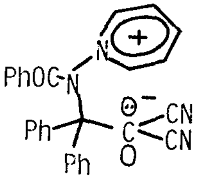
4a; R=H
4b; R=Me

the absorption in the longer wavelength region can be attributed to intramolecular charge transfer transition and a blue shift was observed in cyclohexane [λmax (cyclohexane) 243 nm (logε=3.31), 464 (4.21)]. Its ^{13}C NMR spectrum shows only one peak in higher field than 100 ppm,[6] indicating the presence of one sp^3 carbon. The ^{1}H NMR spectrum is also consistent with this structure.[6] The IR spectrum exhibits two peaks due to CN [νmax (KBr) 2210, 2190 cm^{-1}] as well as a peak due to NH (3280 cm^{-1}). The structure is also supported by following chemical evidence. Treatment of 3a with benzoyl chloride in pyridine gave N-benzoyl derivative 5 (mp 227-229 °C) whose UV spectrum exhibits a characteristic charge transfer band at 431 nm (logε=4.47). This fact shows that the adduct 3a is not a simple π-complex between pyridine N-imide and ylidenemalononitrile 2a because pyridine N-benzoylimide did not react with 2a at all. The reaction of 3a with a few drops of conc. hydrochloric acid in boiling methanol gave benzophenone in high yield. This result indicates the presence of the carbanion moiety stabilized by two cyano groups because ylidenemalononitrile 2a did not afford benzophenone under the same conditions.

On the other hand, the NMR spectrum of another adduct 4a provides convincing evidence for the structural assignment of 4a. Thus, the ^{1}H NMR spectrum shows two methine proton signals mutually coupled at δ4.96 and 5.52 ppm in addition to aromatic proton signals.[7] The ^{13}C NMR spectrum shows two peaks due to sp^3 carbons at δ36.1 and 53.1 ppm.[7] The formation of 4a can be explained by initial 1,3-dipolar cycloaddition of pyridine N-imide to one C≡N bond of 2a to give an intermediate 6 followed by a 1,5-hydrogen shift and a 1,3-hydrogen

Table 1. UV spectra of the dipole compounds 3

Compds	λmax	nm (logε) in ethanol		
3a	240 (4.08)	315 (3.81)	394 (4.88)	514 (4.87)
3b	240 (4.09)	318 (3.88)	508 (4.77)	535 (4.81)
3c	240 (3.95)	300 (3.67)	490 (4.73)	505 (4.72)
3d	236 (4.02)	300 (3.80)	485 (4.80)	502 (4.29)



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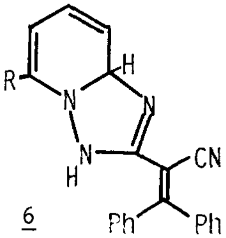

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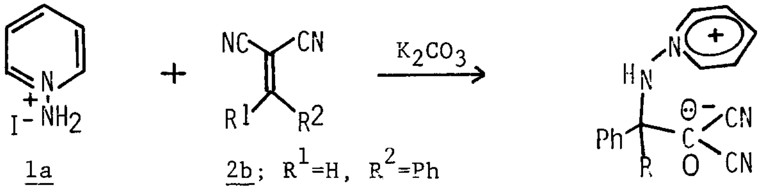
shift for aromatization. This type of hydrogen migration is a new one although the 1,3-dipolar cycloaddition of pyridine N-imides to a C≡N bond is known.[8]

In a similar manner, the reaction of a methyl substituted pyridine N-imide 1b with ylidenemalononitrile 2a led to the formation of a dipole compounds 3b (mp 205-208 °C, 38 %) and a triazolopyridine derivative 4b (mp 173-175 °C, 15 %). Introduction of a methyl substituent results in a red shift of the charge-transfer absorption band as shown in Table 1. The addition reaction is sensitive to the substituents of the ylidenemalononitriles. In the reaction of pyridine N-imide with ylidenemalononitriles 2b and 2c, dipole compounds 3c (mp 210-211 °C, 11 %) and 3d (mp 156-160 °C, 25 %) were obtained, respectively and triazolopyridine derivatives corresponding to 4 could not be identified. This result is rationalized in terms of the lability of ylidenemalononitriles 2b and 2c under the reaction conditions and the steric effect of the phenyl group disturbing the attack of the ylides to the C-C double bond.[9]



1a

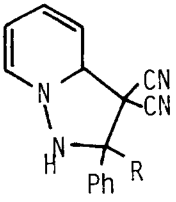
2b; R^1=H, R^2=Ph

2c; R^1=Me, R^2=Ph

3c; R=H

3d; R=Me

To our knowledge, the dipole compounds 3 are first examples of an intramolecular charge-transfer complex between a pyridinium cation and a carbanion although an intermolecular salt is known.[10] They are surprisingly stable upon heating and irradiation, and cyclization to 7 could not be observed. It is also surprising that the nucleophilic reactivity of the carbanion is smaller than that of the amino group as can be seen in the reaction with benzoyl chloride. The stability of 3 may be attributed to the good overlap of the pyridinium cation and the carbanion part as suggested by inspection of the structure using Dreiding models. Further studies are in progress to investigate the properties of these novel compounds.



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References and Notes

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4. Y. Tamura and M. Ikeda, *Adv. Heterocyclic Chem.*, **29**, 71 (1981)
5. Recently much attention has been focused on the chemistry of ylidenemalononitrile from synthetic and mechanistic viewpoints. For reviews of ylidenemalononitriles, F. Freeman, *Chem. Rev.*, **80**, 329 (1980).
6. ^{1}H NMR δppm (DMSO-d_6) 6.05-6.65 (m, 2H), 7.10-7.82 (m, 13H), 10.69 (br s, NH), ^{13}C NMR δppm (DMSO-d_6) 64.8 (s), 103.9 (d), 114.9 (s), 116.2 (d), 116.9 (s), 127.3, 127.5, 128.4, 128.6, 129.4, 129.7, 131.9, 136.8 (s), 148.3 (d), 154.1 (s), 156.6 (d), 160.1 (d).
7. ^{1}H NMR δppm (DMSO-d_6) 4.96 (d, 1H, J=11.0 Hz), 5.52 (d, 1H, J=11.0 Hz), 6.50-7.75 (m, 13 H), 8.64 (dd, J=7.0, 1.5 Hz), ^{13}C NMR δppm (DMSO-d_6) 36.1 (d), 53.1 (d), 114.4 (d), 115.9 (d), 118.3 (s), 126.8 (d), 127.1 (d), 127.7 (d), 128.2 (d), 128.8 (d), 130.4 (d), 140.2 (s), 140.8 (s), 150.7 (s), 160.3 (s).
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9. Reaction of isopropylidenemalononitrile **2d** (R^1=R^2=Me) or cyclohexylidenemalononitrile **2e** [R^1, R^2= -$(CH_2)_5$-] gave a complex mixture. At least one phenyl group is needed for the formation of the stable dipole compounds.
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