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The pyrolysis of 2-azidopyrazines led to give 1-cyanoimidazoles, which were hydrolyzed in alkaline and acidic media to the corresponding imidazoles. This ring transformation occurred also by photolysis.

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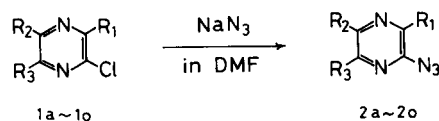
Ring transformation of pyrazines to imidazoles can already be performed by various types of reactions [1-5], and we reported briefly the pyrolytic transformation of azido-diphenylpyrazines to the corresponding diphenylimidazoles in an earlier paper [6]. The present paper constitutes a continuation of our study on the ring contraction of azidopyrazines and described the pyrolytic and photolytic transformation of some other azidopyrazines to the corresponding imidazoles.

In order to prepare the azidopyrazines, the replacement of the chlorine atoms on the pyrazine ring with an azido group was achieved under heating with two equivalents of sodium azide in *N,N*-dimethylformamide as already reported [6]. Among the starting chloropyrazines, an unknown 2-chloropyrazine, 2-chloro-3,6-dibutylpyrazine (**1e**), was derived from DL-3,6-dibutyl-2,5-piperazinedione by treatment with phosphoryl chloride [7]. Azidopyrazines were purified by silica gel column chromatography and were obtained in satisfactory yields, as shown in Table I.

The structures of 2-azidopyrazine and 2-azido-5,6-diphenylpyrazine (**2m**) were already discussed by two groups [4,8]. These substances were found to take a tetrazolo form always in a solid state and to be existent in an equilibrium between azido and tetrazolo forms in chloroform and tetrahydrofuran solutions. In the previous paper [6], we suggested that all the azidodiphenylpyrazines are existent exclusively as tetrazolo[1,5-*c*]pyrazines in solid states and that only the ir spectra of the 2-azidodiphenylpyrazines carrying a phenyl group at C-6 indicate azide bands in chloroform solutions. These phenomena were also observed in the present work. Namely, the ir spectrum of 2-azido-3-methyl-6-phenylpyrazine (**2i**) indicated a strong band characteristic of an azido group only in chloroform solutions. Since the other azidopyrazines prepared in the present work showed no such bands both in solid states and chloroform solutions, these azidopyrazines may be existent always in tetrazolo forms.

All the azidopyrazines thus obtained were subjected to a

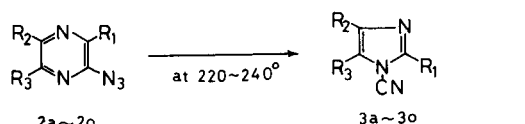
Table I
Preparation of Azidopyrazines



	Compound 1			Reaction Temperature (°C)	Time (hours)	Product 2	Yield %
	R ₁	R ₂	R ₃				
1a [9,10]	Me	H	Me	reflux	10	2a	83
1b [11]	Et	H	Et	reflux	10	2b	70
1c [12]	Pr	H	Pr	reflux	10	2c	66
1d [12]	<i>i</i> -Pr	H	<i>i</i> -Pr	reflux	10	2d	76
1e	Bu	H	Bu	reflux	10	2e	84
1f [13]	<i>i</i> -Bu	H	<i>i</i> -Bu	reflux	10	2f	72
1g [9]	<i>s</i> -Bu	H	<i>s</i> -Bu	reflux	10	2g	81
1h [14]	H	Ph	Me	120	5	2h	71
1i [7]	Me	H	Ph	120	5	2i	64
1j [7]	Ph	H	Me	120	12	2j	33
1k [15]	Me	Ph	H	120	5	2k	71
1l [15]	Ph	Me	H	120	5	2l	73
1m [10]	H	Ph	Ph	150	5	2m [4,6]	81
1n [16]	Ph	H	Ph	120	24	2n [6]	62
1o [16]	Ph	Ph	H	130	5	2o [6]	81

pyrolysis under the same conditions as reported [6]. The reaction was finished in a moment after an explosive generation of nitrogen gas, and the corresponding 1-cyanoimidazoles were obtained in excellent yields, as shown in Table II.

Table II
Pyrolysis of Azidopyrazines



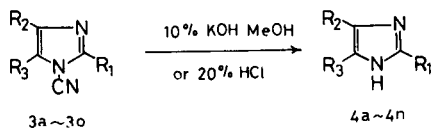
Compound 2	Compound 2			Product 3	Yield %
	R ₁	R ₂	R ₃		
2a	Me	H	Me	3a	89
2b	Et	H	Et	3b	93
2c	Pr	H	Pr	3c	91
2d	<i>i</i> -Pr	H	<i>i</i> -Pr	3d	96
2e	Bu	H	Bu	3e	90
2f	<i>i</i> -Bu	H	<i>i</i> -Bu	3f	93
2g	<i>s</i> -Bu	H	<i>s</i> -Bu	3g	88
2h	H	Ph	Me	3h	92
2i	Me	H	Ph	3i	89
2j	Ph	H	Me	3j	74
2k	Me	Ph	H	3k	90
2l	Ph	Me	H	3l	76
2m [4,6]	H	Ph	Ph	3m [4,6]	92
2n [6]	Ph	H	Ph	3n [6]	91
2o [6]	Ph	Ph	H	3o [6]	91

The hydrolysis of the 1-cyanoimidazoles led to the imidazoles. This hydrolysis occurred both in alkaline and acidic media. However, the yields of the desired imidazoles by alkaline hydrolysis were better than those in the case of acidic hydrolysis.

The photolysis of azidopyrazines was also investigated. The benzene, ethanol, and hexane solutions of azidodiphenylpyrazines and azidomethylphenylpyrazines were irradiated for 30 minutes, using a 400W high-pressure mercury lamp accompanied with a pyrex cooling jacket. However, only resinous products were obtained in all solvents.

The photolytic ring transformation of 2-azido-3,6-dialkylpyrazines occurred successfully in ethanol solutions. On the other hand, only the unreacted starting materials were recovered in the other two solvents. The spots of the 2-azido-3,6-dialkylpyrazines on the tlc plates (Wakogel B-5) were no longer observed on tlc analysis of reaction mixtures after 2 hours of irradiation in ethanol solutions and the photoproducts, 1-cyanoimidazoles and imidazoles, were separated from each other by silica gel column chromatography. As shown in Table IV, a long irradiation increased the yields of imidazoles. Since 1-cyanoimidazoles were ascertained to be transformed quantitatively to the corresponding imidazoles by the irradiation, it may be concluded that the photolysis of 2-azido-3,6-dialkylpyrazines led to the 2,4-dialkylimidazoles *via* the 1-cyano-2,4-dialkylimidazoles. However, the mechanism of the loss of the cyano group was left undetermined.

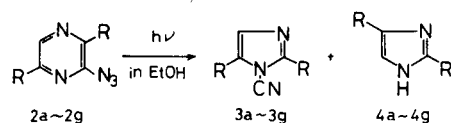
Table III
Hydrolysis of 1-Cyanoimidazoles



R ₁	Compound 3			Product 4 [a]	Yield %
	R ₂	R ₃			
3a	Me	H	Me	4a [17]	89 (80 [b])
3b	Et	H	Et	4b [18]	92 (82 [b])
3c	Pr	H	Pr	4c [18]	91 (69 [b])
3d	<i>i</i> -Pr	H	<i>i</i> -Pr	4d [18]	89 (78 [b])
3e	Bu	H	Bu	4e	93 (85 [b])
3f	<i>i</i> -Bu	H	<i>i</i> -Bu	4f	95 (84 [b])
3g	<i>s</i> -Bu	H	<i>s</i> -Bu	4g	93 (71 [b])
3h	H	Ph	Me	4h [19]	90
3i	Me	H	Ph	4i [17]	96
3j	Ph	H	Me	4j [20]	93
3k	Me	Ph	H	4i [17]	93
3l	Ph	Me	H	4j [20]	96
3m	H	Ph	Ph	4m [6,19]	91 (78 [b])
3n	Ph	Ph	H	4n [6,17]	88 (80 [b])
3o	Ph	H	Ph	4n [6,17]	89 (81 [b])

[a] Since the position of the proton on the imidazole ring was not made clear, the structures were given tentatively. [b] Acid hydrolysis.

Table IV
Photolysis of Azidopyrazines



Compound 2	R	Product 3	Yield %	Product 4 [a]	Yield %
2b	R = Et	3b	61	4b [18]	35
2c	R = Pr	3c	58	4c [18]	33
2d	R = <i>i</i> -Pr	3d	59	4d [18]	38
2e	R = Bu	3e	60	4e	30
2f	R = <i>i</i> -Bu	3f	52	4f	36
2g	R = <i>s</i> -Bu	3g	67	4g	25

[a] Since the position of the proton on the imidazole ring was not made clear, the structures were given tentatively.

Chloropyrazines can be prepared without difficulty, and therefore, the pyrolysis of azidopyrazines might be an excellent method for preparation of some imidazoles.

EXPERIMENTAL

Melting points were recorded on a Yanagimoto micro-melting point apparatus and are uncorrected. Boiling points are also uncorrected. All uv spectra were taken in 95% ethanol using Hitachi Model 323 and 557 spectrophotometers, ir spectra on a Shimadzu IR-400 spectrometer, and pmr spectra in deuteriochloroform using JEOL PS-100 and Varian EM-360 instruments with tetramethylsilane as an internal standard. Mass spectra were obtained with Hitachi RMU-7L and M-80 spectrometers.

Reaction of 3,6-Dibutyl-2,5-piperazinedione with Phosphoryl Chloride.

A mixture of DL-3,6-dibutyl-2,5-piperazinedione (DL-norleucine anhydride) (11.3 g, 0.05 mole) [21], phosphoryl chloride (20 ml), and phosphorus pentachloride (2 g) was heated at 140° for 1 hour in a sealed tube. After cooling, the mixture was poured into ice water, made alkaline with potassium carbonate, and extracted with hexane. The hexane solution was extracted with concentrated hydrochloric acid. The water layer was made alkaline with potassium carbonate, extracted with ether, and removal of ether gave 2-chloro-3,6-dibutylpyrazine (1e) (7.49 g, 66%) as an oil. The usual work-up of the hexane layer afforded 3,6-dibutyl-2,5-dichloropyrazine (2.24 g, 17%) as a colorless oil.

2-Chloro-3,6-dibutylpyrazine (1e).

This compound had the following physical properties: bp 114-116°/4 torr (colorless oil); uv: λ max 213 (log ϵ = 3.93), 280 (3.81), 300.5 (3.48, shoulder) nm; pmr: δ 0.88 (6H, t, J = 8 Hz, 2 \times CH₂CH₂CH₂CH₃), 1.20-1.88 (8H, m, 2 \times CH₂CH₂CH₂CH₃), 2.68 (2H, t, J = 8 Hz, CH₂CH₂CH₂CH₃), 2.86 (2H, t, J = 8 Hz, CH₂CH₂CH₂CH₃), 8.21 (1H, s, pyrazine H) ppm; ms: m/e 226 (M⁺), 183 (M⁺ - C₃H₇), 140 (M⁺ - 2C₃H₇).

Anal. Calcd. for C₁₂H₁₉ClN₂: C, 63.56; H, 8.45; N, 12.36. Found: C, 63.31; H, 8.48; N, 12.26.

3,6-Dibutyl-2,5-dichloropyrazine.

This compound had the following physical properties: bp 132°/4 torr; uv: λ max 221 (log ϵ = 4.24), 279 (3.96, shoulder), 297 (4.12) nm; pmr: δ 0.96 (6H, t, J = 6 Hz, 2 \times CH₂CH₂CH₂CH₃), 1.26-1.88 (8H, m, 2 \times CH₂CH₂CH₂CH₃), 2.89 (4H, t, J = 6 Hz, 2 \times CH₂CH₂CH₂CH₃), ppm; ms: m/e 260 (M⁺), 218 (M⁺ - C₃H₇), 175 (M⁺ - C₃H₇ - C₃H₇).

Anal. Calcd. for C₁₂H₁₈Cl₂N₂: C, 55.18; H, 6.95; N, 10.73. Found: C, 54.89; H, 6.80; N, 10.58.

General Procedure for Preparation of Azidopyrazines (2a-o).

A suspension of a 2-chloropyrazine (50 mmoles) and sodium azide (90% purity, 7.25 g, 100 mmoles) in *N,N*-dimethylformamide (100 ml) was heated on an oil bath under the conditions as illustrated in Table I. The reaction mixture was concentrated to dryness *in vacuo* to give an oily residue, which was triturated with water and extracted with ether. Evaporation of the solvent afforded the 2-azidopyrazine as a dark brown oil or crystalline mass. Purification of the crude azidopyrazines was made by chromatography on silica gel (Wakogel C-200, 20-30 g), eluting with a mixture of hexane and methylene chloride (1:1), and by the following distillation or recrystallization from methanol to furnish colorless oils or needles.

2-Azido-3,6-dimethylpyrazine (2a).

This compound had the following physical properties: mp 130-131°; uv: λ max 275 (log ϵ = 3.90) nm; pmr: δ 2.78 (3H, s, CH₃), 2.90 (3H, s, CH₃), 7.88 (1H, s, pyrazine H) ppm; ms: m/e 149 (M⁺), 121 (M⁺ - N₂).

Anal. Calcd. for C₆H₈N₃: C, 48.31; H, 4.73; N, 46.96. Found: C, 48.14; H, 4.73; N, 47.22.

2-Azido-3,6-diethylpyrazine (2b).

This compound had the following physical properties: mp 70-71°; uv: λ max 272 (log ϵ = 3.93) nm; pmr: δ 1.25 (3H, t, J = 8 Hz, CH₂CH₃), 1.32 (3H, t, J = 8 Hz, CH₂CH₃), 3.30 (2H, q, J = 8 Hz, CH₂CH₃), 3.40 (2H, q, J = 8 Hz, CH₂CH₃), 7.96 (1H, s, pyrazine H) ppm; ms: m/e 177 (M⁺), 149 (M⁺ - N₂).

Anal. Calcd. for C₈H₁₁N₃: C, 54.22; H, 6.26; N, 39.52. Found: C, 54.15;

H, 6.37; N, 39.58.

2-Azido-3,6-dipropylpyrazine (2c).

This compound had the following physical properties: bp 120°/1 torr; uv: λ max 275 (log ϵ = 3.94) nm; pmr: δ 1.00 (3H, t, J = 7 Hz, CH₂CH₂CH₃), 1.03 (3H, t, J = 7 Hz, CH₂CH₂CH₃), 1.93 (4H, m, 2 \times CH₂CH₂CH₃), 3.23 (2H, t, J = 7 Hz, CH₂CH₂CH₃), 3.33 (2H, t, J = 7 Hz, CH₂CH₂CH₃), 7.97 (1H, s, pyrazine H) ppm; ms: m/e 205 (M⁺), 148 (M⁺ - N₂ - C₂H₅).

Anal. Calcd. for C₁₀H₁₅N₃: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.49; H, 7.21; N, 34.20.

2-Azido-3,6-diisopropylpyrazine (2d).

This compound had the following physical properties: mp 59-61°; uv: λ max 275 (log ϵ = 3.92) nm; pmr: δ 1.52 (6H, d, J = 6 Hz, CH(CH₃)₂), 1.57 (6H, d, J = 6 Hz, CH(CH₃)₂), 3.85 (2H, m, 2 \times CH(CH₃)₂), 8.02 (1H, s, pyrazine H) ppm; ms: m/e 205 (M⁺), 177 (M⁺ - N₂).

Anal. Calcd. for C₁₀H₁₅N₃: C, 58.51; H, 7.37; N, 34.12. Found: C, 58.39; H, 7.28; N, 34.41.

2-Azido-3,6-dibutylpyrazine (2e).

This compound had the following physical properties: bp 128-131°/1 torr; uv: λ max 212 (log ϵ = 3.88), 279 (3.82) nm; pmr: δ 1.07 (6H, t, J = 5 Hz, 2 \times CH₂CH₂CH₂CH₃), 1.27-2.20 (8H, m, 2 \times CH₂CH₂CH₂CH₃), 3.33 (2H, t, J = 8 Hz, CH₂CH₂CH₂CH₃), 3.42 (2H, t, J = 8 Hz, CH₂CH₂CH₂CH₃), 7.90 (1H, s, pyrazine H) ppm; ms: m/e 233 (M⁺), 176 (M⁺ - C₂H₅).

Anal. Calcd. for C₁₂H₁₉N₃: C, 61.77; H, 8.21; N, 30.02. Found: C, 62.03; H, 8.40; N, 29.98.

2-Azido-3,6-diisobutylpyrazine (2f).

This compound had the following physical properties: mp 101-103°; uv: λ max 282 (log ϵ = 3.93) nm; pmr: δ 0.93 (12H, d, J = 8 Hz, 2 \times CH₂CH(CH₃)₂), 2.58 (2H, m, 2 \times CH₂CH(CH₃)₂), 2.97 (2H, d, J = 7 Hz, CH₂CH(CH₃)₂), 3.10 (2H, d, J = 7 Hz, CH₂CH(CH₃)₂), 8.37 (1H, s, pyrazine H) ppm; ms: m/e 233 (M⁺), 203 (M⁺ - N₂).

Anal. Calcd. for C₁₂H₁₉N₃: C, 61.77; H, 8.21; N, 30.02. Found: C, 61.70; H, 8.06; N, 30.10.

2-Azido-3,6-di-sec-butylpyrazine (2g).

This compound had the following physical properties: bp 124-126°/1 torr; uv: λ max 277 (log ϵ = 3.92) nm; pmr: δ 0.73 (3H, t, J = 6 Hz, CH(CH₃)CH₂CH₃), 0.83 (3H, t, J = 6 Hz, CH(CH₃)CH₂CH₃), 1.37 (6H, dd, J = 6 Hz, 2 \times CH(CH₃)CH₂CH₃), 3.23 (1H, m, J = 6 Hz, CH(CH₃)CH₂CH₃), 3.63 (1H, m, J = 6 Hz, CH(CH₃)CH₂CH₃), 7.73 (1H, s, pyrazine H) ppm; ms: m/e 233 (M⁺), 190 (M⁺ - N₂ - CH₃), 176 (M⁺ - N₂ - C₂H₅).

Anal. Calcd. for C₁₂H₁₉N₃: C, 61.77; H, 8.21; N, 30.02. Found: C, 61.92; H, 8.49; N, 30.12.

2-Azido-6-methyl-5-phenylpyrazine (2h).

This compound had the following physical properties: mp 124-125°; uv: λ max 242 (log ϵ = 4.21), 271 (4.06), 305 (3.67, shoulder) nm; pmr: δ 3.13 (3H, s, CH₃), 7.60 (5H, m, benzene H), 9.58 (1H, s, pyrazine H) ppm; ms: m/e 211 (M⁺), 183 (M⁺ - N₂).

Anal. Calcd. for C₁₁H₉N₃: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.27; H, 4.20; N, 33.29.

2-Azido-3-methyl-6-phenylpyrazine (2i).

This compound had the following physical properties: mp 130-131°; uv: λ max 232 (log ϵ = 3.91, shoulder), 268 (3.87, shoulder), 307 (4.11) nm; ir (chloroform): 2120 cm⁻¹ (ν N₃); pmr: δ 3.07 (3H, s, CH₃), 7.57 (3H, m, benzene H), 8.00 (2H, m, benzene H), 8.27 (1H, s, pyrazine H) ppm; ms: m/e 211 (M⁺), 183 (M⁺ - N₂).

Anal. Calcd. for C₁₁H₉N₃: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.49; H, 4.31; N, 33.21.

2-Azido-6-methyl-3-phenylpyrazine (2j).

This compound had the following physical properties: mp 199-200°;

uv: λ max 235 (log ϵ = 3.68), 261 (3.87, shoulder), 310 (4.30), 317 (4.31), 336 (3.98, shoulder) nm; pmr: δ 2.98 (3H, s, CH₃), 7.55 (3H, m, benzene H), 8.13 (1H, s, pyrazine H), 8.77 (2H, m, benzene H) ppm; ms: m/e 211 (M⁺), 183 (M⁺ - N₂).

Anal. Calcd. for C₁₁H₉N₃: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.46; H, 4.22; N, 33.43.

2-Azido-3-methyl-5-phenylpyrazine (2k).

This compound had the following physical properties: mp 205-206°; uv: λ max 221 (log ϵ = 4.06), 240 (4.32) nm; pmr: δ 3.20 (3H, s, CH₃), 7.50 (3H, m, benzene H), 8.00 (2H, m, benzene H), 8.90 (1H, s, pyrazine H) ppm; ms: m/e 211 (M⁺), 183 (M⁺ - N₂).

Anal. Calcd. for C₁₁H₉N₃: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.29; H, 4.16; N, 33.43.

2-Azido-5-methyl-3-phenylpyrazine (2l).

This compound had the following physical properties: mp 142-143°; uv: λ max 221.5 (log ϵ = 4.64), 240 (4.48), 263 (3.70, shoulder) nm; pmr: δ 3.20 (3H, s, CH₃), 7.53 (3H, m, benzene H), 8.00 (2H, m, benzene H), 8.95 (1H, s, pyrazine H) ppm; ms: m/e 211 (M⁺), 183 (M⁺ - N₂).

Anal. Calcd. for C₁₁H₉N₃: C, 62.55; H, 4.30; N, 33.16. Found: C, 62.35; H, 4.41; N, 33.19.

2-Azido-3,6-diphenylpyrazine (2n).

This compound had the following physical properties: mp 159-160°; uv: λ max 238 (log ϵ = 4.17, shoulder), 280 (4.05, shoulder), 343 (4.16) nm; ir (chloroform): 2145 cm⁻¹ (ν N₃); pmr: δ 7.32-8.03 (10H, broad m, benzene H), 8.60 (1H, s, pyrazine H) ppm; ms: m/e 273 (M⁺), 245 (M⁺ - N₂).

Anal. Calcd. for C₁₆H₁₁N₃: C, 70.31; H, 4.06; N, 25.63. Found: C, 70.18; H, 4.05; N, 25.49.

2-Azido-3,5-diphenylpyrazine (2o).

This compound had the following physical properties: mp 170-171°; uv: λ max 238 (log ϵ = 4.17, shoulder), 278 (4.03, shoulder), 343 (4.61) nm; pmr: δ 7.67 (6H, m, benzene H), 8.20 (4H, m, benzene H), 9.10 (1H, s, pyrazine H) ppm; ms: m/e 273 (M⁺), 245 (M⁺ - N₂).

Anal. Calcd. for C₁₆H₁₁N₃: C, 70.31; H, 4.06; N, 25.63. Found: C, 70.26; H, 4.01; N, 25.79.

General Procedure for Preparation of 1-Cyanoimidazoles by Pyrolysis.

a) 1-Cyano-2,5-dialkylimidazoles.

A 2-azido-3,6-dialkylpyrazine (3-5 g) was heated at 240° on a metal bath for 30-60 seconds. After ceasing of nitrogen generation, the crude 1-cyanoimidazole was distilled under a reduced pressure to give a 1-cyano-2,5-dialkylimidazole as a colorless oil.

b) 1-Cyanodiphenyl- and 1-Cyanomethylphenylimidazoles.

A 2-azidodiphenylpyrazine or 2-azidomethylphenylpyrazine (200-300 mg) was heated at 220° on a metal bath. The pyrolysis finished in a moment with an explosive generation of nitrogen gas. The product was chromatographed on silica gel (Wakogel C-200) with methylene chloride to give the corresponding 1-cyanoimidazole as a pale yellow solid or colorless oil.

Irradiation of 2-Azidopyrazines.

A 2-azidopyrazine (1 mmole) was dissolved in ethanol (250 ml) and irradiated under an atmosphere of air for 2 hours, using a 400W high-pressure mercury lamp equipped with a pyrex cooling jacket. The solvent was then distilled off *in vacuo*, and the residue was chromatographed on silica gel (Wakogel C-200, 10 g), using methylene chloride and ethyl acetate as the eluents. The methylene chloride fractions gave the 1-cyanoimidazole and the ethyl acetate fractions afforded the corresponding imidazole.

1-Cyano-2,5-dimethylimidazole (3a).

This compound had the following physical properties: mp 125-126° (from hexane); uv: λ max 232 (log ϵ = 4.01) nm; ir (potassium bromide): 2260 cm⁻¹ (ν C \equiv N); pmr: δ 1.94 (3H, s, CH₃), 3.06 (3H, s, CH₃), 6.60 (1H, s, imidazole H) ppm; ms: m/e 121 (M⁺), 120 (M⁺ - H).

Anal. Calcd. for C₆H₇N₃: C, 59.49; H, 5.82; N, 34.69. Found: C, 59.25; H, 6.09; N, 34.36.

1-Cyano-2,5-diethylimidazole (3b).

This compound had the following physical properties: bp 100°/12 torr; uv: λ max 232 (log ϵ = 4.06) nm; ir (liquid film): 2260 cm⁻¹ (ν C \equiv N); pmr: δ 1.18 (3H, t, J = 8 Hz, CH₂CH₃), 1.34 (3H, t, J = 8 Hz, CH₂CH₃), 2.50 (2H, q, J = 8 Hz, CH₂CH₃), 2.82 (2H, q, J = 8 Hz, CH₂CH₃), 6.76 (1H, s, imidazole H) ppm; ms: m/e 149 (M⁺), 134 (M⁺ - CH₃).

Anal. Calcd. for C₈H₁₁N₃: C, 64.40; H, 7.43; N, 28.17. Found: C, 64.08; H, 7.31; N, 27.89.

1-Cyano-2,5-dipropylimidazole (3c).

This compound had the following physical properties: bp 86-89°/3 torr; uv: λ max 232 (log ϵ = 4.01) nm; ir (liquid film): 2275 cm⁻¹ (ν C \equiv N); pmr: δ 1.00 (6H, t, J = 6 Hz, 2 \times CH₂CH₂CH₃), 1.67 (4H, m, J = 6 Hz, 2 \times CH₂CH₂CH₃), 2.58 (2H, t, J = 6 Hz, CH₂CH₂CH₃), 2.75 (2H, t, J = 6 Hz, CH₂CH₂CH₃), 6.55 (1H, s, imidazole H) ppm; ms: m/e 177 (M⁺), 162 (M⁺ - CH₃).

Anal. Calcd. for C₁₀H₁₅N₃: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.95; H, 8.76; N, 24.02.

1-Cyano-2,5-diisopropylimidazole (3d).

This compound had the following physical properties: bp 60°/9 torr; uv: λ max 232 (log ϵ = 4.08) nm; ir (liquid film): 2260 cm⁻¹ (ν C \equiv N); pmr: δ 1.27 (6H, d, J = 6 Hz, CH(CH₃)₂), 1.37 (6H, d, J = 6 Hz, CH(CH₃)₂), 2.98 (1H, m, CH(CH₃)₂), 3.14 (1H, m, CH(CH₃)₂), 6.52 (1H, s, imidazole H) ppm; ms: m/e 177 (M⁺), 162 (M⁺ - CH₃).

Anal. Calcd. for C₁₀H₁₅N₃: C, 67.76; H, 8.53; N, 23.71. Found: C, 67.56; H, 8.80; N, 23.67.

1-Cyano-2,5-dibutylimidazole (3e).

This compound had the following physical properties: bp 112-114°/2 torr; uv: λ max 233 (log ϵ = 3.93) nm; ir (liquid film): 2260 cm⁻¹ (C \equiv N); pmr: δ 0.93 (6H, t, J = 8 Hz, 2 \times CH₂CH₂CH₂CH₃), 1.55 (8H, m, 2 \times CH₂CH₂CH₂CH₃), 2.67 (2H, t, J = 7 Hz, CH₂CH₂CH₂CH₃), 2.80 (2H, t, J = 7 Hz, CH₂CH₂CH₂CH₃), 6.58 (1H, s, imidazole H) ppm; ms: m/e 205 (M⁺).

Anal. Calcd. for C₁₂H₁₉N₃: C, 70.20; H, 9.33; N, 20.47. Found: C, 70.38; H, 9.61; N, 20.39.

1-Cyano-2,5-diisobutylimidazole (3f).

This compound had the following physical properties: bp 78-80°/10 torr; uv: λ max 234 (log ϵ = 4.16) nm; ir (liquid film): 2270 cm⁻¹ (ν C \equiv N); pmr: δ 0.90 (6H, d, J = 6 Hz, CH₂CH(CH₃)₂), 0.97 (6H, d, J = 6 Hz, CH₂CH(CH₃)₂), 2.02 (2H, m, 2 \times CH₂CH(CH₃)₂), 2.48 (2H, d, J = 8 Hz, CH₂CH(CH₃)₂), 2.66 (2H, d, J = 8 Hz, CH₂CH(CH₃)₂), 6.60 (1H, s, imidazole H) ppm; ms: m/e 205 (M⁺), 190 (M⁺ - CH₃).

Anal. Calcd. for C₁₂H₁₉N₃: C, 70.20; H, 9.33; N, 20.47. Found: C, 69.90; H, 9.48; N, 20.69.

1-Cyano-2,5-di-sec-butylimidazole (3g).

This compound had the following physical properties: bp 81-83°/1 torr; uv: λ max 233 (log ϵ = 3.96) nm; ir (liquid film): 2270 cm⁻¹ (ν C \equiv N); pmr: δ 0.90 (6H, t, J = 7 Hz, 2 \times CH(CH₃)CH₂CH₃), 1.27 (3H, d, J = 7 Hz, CH(CH₃)CH₂CH₃), 1.33 (3H, d, J = 7 Hz, CH(CH₃)CH₂CH₃), 1.65 (4H, m, 2 \times CH(CH₃)CH₂CH₃), 2.75 (2H, m, 2 \times CH(CH₃)CH₂CH₃), 6.60 (1H, s, imidazole H) ppm; ms: m/e 205 (M⁺), 190 (M⁺ - CH₃).

Anal. Calcd. for C₁₂H₁₉N₃: C, 70.20; H, 9.33; N, 20.47. Found: C, 70.46; H, 9.62; N, 20.30.

1-Cyano-5-methyl-4-phenylimidazole (3h).

This compound had the following physical properties: mp 103-104° (from hexane); uv: λ max 248 (log ϵ = 3.90) nm; ir (potassium bromide): 2270 cm⁻¹ (ν C \equiv N); pmr: δ 2.33 (3H, s, CH₃), 7.52 (5H, s, benzene H), 7.93 (1H, s, imidazole H) ppm; ms: m/e 183 (M⁺).

Anal. Calcd. for C₁₁H₉N₃: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.31; H, 5.03; N, 23.10.

1-Cyano-2-methyl-5-phenylimidazole (3i).

This compound had the following physical properties: bp 111-116°/1 torr; uv: λ max 217 (log ϵ = 4.40), 258 (4.26) nm; ir (liquid film): 2270 cm^{-1} (ν C \equiv N); pmr: δ 2.65 (3H, s, CH₃), 6.98 (1H, s, imidazole H), 7.43 (5H, s, benzene H) ppm; ms: m/e 183 (M⁺).

Anal. Calcd. for C₁₁H₉N₃: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.28; H, 5.16; N, 23.10.

1-Cyano-5-methyl-2-phenylimidazole (3j).

This compound had the following physical properties: mp 58-59° (from hexane); uv: λ max 274 (log ϵ = 4.27) nm; ir (potassium bromide): 2280 cm^{-1} (ν C \equiv N); pmr: δ 2.24 (3H, s, CH₃), 6.86 (1H, s, imidazole H), 7.48 (3H, m, benzene H), 7.90 (2H, m, benzene H) ppm; ms: m/e 183 (M⁺).

Anal. Calcd. for C₁₁H₉N₃: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.23; H, 4.87; N, 23.02.

1-Cyano-2-methyl-4-phenylimidazole (3k).

This compound had the following physical properties: mp 105-106° (from hexane); uv: λ max 252 (log ϵ = 3.77) nm; ir (potassium bromide): 2270 cm^{-1} (ν C \equiv N); pmr: δ 2.60 (3H, s, CH₃), 7.36 (4H, m, benzene H and imidazole H), 7.70 (2H, m, benzene H) ppm; ms: m/e 183 (M⁺).

Anal. Calcd. for C₁₁H₉N₃: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.16; H, 5.01; N, 23.02.

1-Cyano-4-methyl-2-phenylimidazole (3l).

This compound had the following physical properties: bp 129-134°/1 torr; uv: λ max 273 (log ϵ = 4.15) nm; ir (liquid film): 2260 cm^{-1} (ν C \equiv N); pmr: δ 2.33 (3H, s, CH₃), 7.03 (1H, s, imidazole H), 7.50 (3H, m, benzene H), 7.93 (2H, m, benzene H) ppm; ms: m/e 183 (M⁺).

Anal. Calcd. for C₁₁H₉N₃: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.26; H, 5.21; N, 23.09.

1-Cyano-4,5-diphenylimidazole (3m).

This compound had the following physical properties: mp 144-145° (from hexane); uv: λ max 228 (log ϵ = 4.34), 272 (4.03) nm; ir (potassium bromide): 2270 cm^{-1} (ν C \equiv N); pmr: δ 7.24 (3H, m, benzene H), 7.47 (7H, s, benzene H), 7.98 (1H, s, imidazole H) ppm; ms: m/e 245 (M⁺).

Anal. Calcd. for C₁₆H₁₁N₃: C, 78.35; H, 4.52; N, 16.98. Found: C, 78.25; H, 4.57; N, 16.98.

1-Cyano-2,5-diphenylimidazole (3n).

This compound had the following physical properties: mp 135-136° (from hexane); uv: λ max 293 (log ϵ = 4.30) nm; ir (potassium bromide): 2270 cm^{-1} (ν C \equiv N); pmr: δ 7.45 (7H, m, benzene H and imidazole H), 7.86 (4H, m, benzene H) ppm; ms: m/e 245 (M⁺).

Anal. Calcd. for C₁₆H₁₁N₃: C, 78.35; H, 4.52; N, 16.98. Found: C, 78.18; H, 4.53; N, 17.26.

1-Cyano-2,4-diphenylimidazole (3o).

This compound had the following physical properties: mp 118-119° (from hexane); uv: λ max 242 (log ϵ = 4.48) nm; ir (potassium bromide): 2270 cm^{-1} (ν C \equiv N); pmr: δ 7.40 (7H, m, benzene H and imidazole H), 7.78 (2H, m, benzene H), 8.00 (2H, m, benzene H) ppm; ms: m/e 245 (M⁺).

Anal. Calcd. for C₁₆H₁₁N₃: C, 78.35; H, 4.52; N, 16.98. Found: C, 78.30; H, 4.43; N, 17.18.

Hydrolysis of 1-Cyanoimidazoles to Imidazoles.

a) An emulsion of a 1-cyanoimidazole (10 mmoles) in a mixture of 10% potassium hydroxide (100 ml) and methanol (100 ml) was stirred at room temperature for 12-14 hours, concentrated to ca. 90-100 ml *in vacuo*, and extracted with methylene chloride. Removal of the solvent afforded the corresponding imidazole as a colorless oil or colorless powders, which were purified by distillation under a reduced pressure or recrystallization from ethyl acetate to furnish a colorless oil or colorless needles.

b) A solution of a 1-cyanoimidazole (10 mmoles) in 20% hydrochloric acid (50 ml) was refluxed for 6 hours. After cooling, the reaction mixture was made alkaline with potassium carbonate, and extracted with methylene chloride to give the corresponding imidazole as a slightly yellow oil or solid.

2,4-Dibutylimidazole (4e).

This compound had the following physical properties: bp 138-141°/1 torr; uv: λ max 213 (log ϵ = 4.11) nm; pmr: δ 0.87 (6H, t, J = 5 Hz, 2 \times CH₂CH₂CH₂CH₃), 1.43 (8H, m, 2 \times CH₂CH₂CH₂CH₃), 2.50 (2H, t, J = 8 Hz, CH₂CH₂CH₂CH₃), 2.63 (2H, t, J = 8 Hz, CH₂CH₂CH₂CH₃), 6.43 (1H, s, imidazole H), 7.80 (1H, broad s, NH) ppm; ms: m/e 180 (M⁺), 138 (M⁺-C₂H₆).

Anal. Calcd. for C₁₁H₂₀N₂: C, 73.28; H, 11.18; N, 15.54. Found: C, 72.98; H, 11.36; N, 15.56.

2,4-Diisobutylimidazole (4f).

This compound had the following physical properties: bp 145°/5 torr; uv: λ max 213 (log ϵ = 4.04) nm; pmr: δ 0.90 (12H, d, J = 6 Hz, 2 \times CH₂CH(CH₃)₂), 1.93 (2H, m, 2 \times CH₂CH(CH₃)₂), 2.38 (2H, d, J = 7 Hz, CH₂CH(CH₃)₂), 2.55 (2H, d, J = 7 Hz, CH₂CH(CH₃)₂), 6.67 (1H, s, imidazole H), 9.27 (1H, broad s, NH) ppm; ms: m/e 180 (M⁺), 138 (M⁺-C₂H₆).

Anal. Calcd. for C₁₁H₂₀N₂: C, 73.28; H, 11.18; N, 15.54. Found: C, 73.51; H, 11.29; N, 15.58.

2,4-Di-sec-butylimidazole (4g).

This compound had the following physical properties: bp 121-125°/1 torr; uv: λ max 212 (log ϵ = 3.96) nm; pmr: δ 0.83 (6H, t, J = 8 Hz, 2 \times CH(CH₃), CH₂CH₃), 1.15 (3H, d, J = 8 Hz, CH(CH₃)CH₂CH₃), 1.22 (3H, d, J = 8 Hz, CH(CH₃)CH₂CH₃), 1.50 (4H, m, 2 \times CH(CH₃)CH₂CH₃), 2.70 (2H, m, 2 \times CH(CH₃)CH₂CH₃), 6.60 (1H, s, imidazole H), 8.20 (1H, broad s, NH) ppm; ms: m/e 180 (M⁺), 165 (M⁺-CH₃).

Anal. Calcd. for C₁₁H₂₀N₂: C, 73.28; H, 11.18; N, 15.54. Found: C, 73.36; H, 11.31; N, 15.71.

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