

ON THE NITRATION OF 5-PHENYL- AND 3-METHYL-5-PHENYLISOXAZOLES

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Abstract - The nitration of the title compounds **1** and **2** with $\text{HNO}_3\text{-H}_2\text{SO}_4$ was reexamined; 4-nitro-5-phenylisoxazole (**3**) and 3-methyl-4-nitro-5-phenylisoxazole (**4**) were obtained by treatment of **1** and **2** with HNO_3 in acetic anhydride under mild conditions.

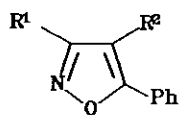
The nitration of 5-phenylisoxazoles has been studied thoroughly in order to establish the nature of the reaction products.¹⁻⁴ Nevertheless, a recent review on nitroisoxazoles⁵ indicates contradictory statements in the literature about the nitro compounds derived from the reaction of 5-phenylisoxazole (**1**) with $\text{HNO}_3\text{-H}_2\text{SO}_4$. Whereas Kochetkov and Khomutova¹ claimed that compound **1** yields both 4-nitro-5-phenylisoxazole (**3**) and 5-*p*-nitrophenylisoxazole (**5a**), Lynch and Shiu² reported that compound **5a** was the sole mononitro product and that is further nitrated to **6a**; these latter results were confirmed by Sokolov and Yuditseva³ which showed that the reaction mixture contained **5a** as the main product together with a little amount of 5-*m*-nitrophenyl- (**5b**) and 4-nitro-5-*p*-nitrophenylisoxazole (**6a**).

Following our interest in the 4-nitroisoxazoles,⁶ we required the still unknown derivatives **3** and **4**; we therefore investigated again the nitration of compounds **1** and **2** with different nitrating agents.

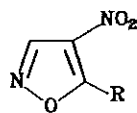
In order to avoid the presence of regioisomers in the starting materials, we prepared compounds **1** and **2** by univocal methods according to Moureu⁷ and Ceresole,⁸ respectively. Several repetitions of Kochetkov and Khomutova's experiment under the same conditions (See Experimental) always gave a solid containing a 1:1:1 mixture of the mononitro derivatives **5a-c** as the predominant component together with minor amounts of the dinitro compounds **6a,b**, which were separated by flash chromatography.

The presence of three compounds in the main reaction product (single spot in tlc) was revealed by an accurate high-field ¹H-nmr analysis (Table 1). The spectrum showed three signals at δ 6.723, 6.703 and 6.517 ppm easily

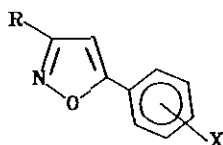
attributable to the protons at position 4 of the isoxazole nucleus of compounds **5a-c**, respectively, which resonate at low frequency with respect to the aromatic ones and appear as doublets owing to the coupling with H-3. Fractional crystallizations from methanol led us to obtain analytically pure isomer **5a**, whereas compounds **5b** and **5c** were isolated at ca. 90% of purity due to their very similar physico-chemical properties.



- 1 $R^1 = R^2 = H$
- 2 $R^1 = Me, R^2 = H$
- 3 $R^1 = H, R^2 = NO_2$
- 4 $R^1 = Me, R^2 = NO_2$



- 6a $R = p-NO_2-C_6H_4$
- 6b $R = m-NO_2-C_6H_4$



| | R | X |
|----|----|--------------------|
| 5a | H | 4'-NO ₂ |
| 5b | H | 3'-NO ₂ |
| 5c | H | 2'-NO ₂ |
| 7a | Me | 4'-NO ₂ |
| 7b | Me | 3'-NO ₂ |
| 7c | Me | 2'-NO ₂ |

The structures of compounds **6a** and **6b**, containing two NO₂ groups (mass spectra), follow from their ¹H-nmr patterns for which no H-4 resonance was observed between δ 6.0 and 7.0. Furthermore, whereas the former shows a characteristic AA'BB' pattern for the phenyl protons, thus proving the *para* position of the aromatic nitro group, the latter, as well as that of compound **5b**, is more complex. Selective homonuclear decoupling experiments and chemical shift arguments (Table 1) led us to formulate compounds **5b** and **6b** as 5-*m*-nitrophenyl- and 4-nitro-5-*m*-nitrophenylisoxazole, respectively.

When 3-methyl-5-phenylisoxazole (**2**) was allowed to react under the same conditions, we obtained a solid containing the *p*-, *m*-, and *o*-nitrophenyl derivatives (**7a-c**); dinitro compounds were now completely absent.

Table 1. ^1H -nmr data of compounds 1-7, 9-11

| Compound | ^1H -nmr (δ , ppm, CDCl_3) |
|----------|--|
| 1 | 6.528 (d, 1H, $^3\text{J}_{\text{H4-H3}} = 1.9$ Hz, 4-H), 7.430-7.510 (m, 3H, ArH ₃), 7.780-7.820 (m, 2H, ArH ₂), 8.295 (d, 1H, $^3\text{J}_{\text{H3-H4}} = 1.9$ Hz, 3-H) |
| 2 | 2.362 (s, 3H, 3-Me), 6.370 (s, 1H, 4-H), 7.434-7.462 (m, 3H, ArH ₃), 7.746-7.778 (m, 2H, ArH ₂) |
| 3 | 7.547-7.644 (m, 3H, ArH ₃), 7.997-8.030 (m, 2H, ArH ₂), 8.888 (s, 1H, 3-H) |
| 4 | 2.635 (s, 3H, 3-Me), 7.557-7.627 (m, 3H, ArH ₃), 7.889-7.922 (m, 2H, ArH ₂) |
| 5a | 6.723 (d, 1H, $^3\text{J}_{\text{H4-H3}} = 1.9$ Hz, 4-H), 8.171 (m AA'BB', 4H, ArH ₄), 8.381 (d, 1H, $^3\text{J}_{\text{H3-H4}} = 1.9$ Hz, 3-H) |
| 5b | 6.703 (d, 1H, $^3\text{J}_{\text{H4-H3}} = 1.9$ Hz, 4-H), 7.700 (dd, 1H, $^3\text{J}_{\text{H5'-H4'}} = 8.3$ Hz, $^3\text{J}_{\text{H5'-H6'}} = 7.8$ Hz, 5'-H), 8.150 (ddd, 1H, $^3\text{J}_{\text{H6'-H5'}} = 7.8$ Hz, $^4\text{J}_{\text{H6'-H2'}} = 1.8$ Hz, $^4\text{J}_{\text{H6'-H4'}} = 1.0$ Hz, 6'-H), 8.310 (ddd, 1H, $^3\text{J}_{\text{H4'-H5'}} = 8.3$ Hz, $^4\text{J}_{\text{H4'-H2'}} = 2.1$ Hz, $^4\text{J}_{\text{H4'-H6'}} = 1.0$ Hz, 4'-H), 8.375 (d, 1H, $^3\text{J}_{\text{H3-H4}} = 1.9$ Hz, 3-H), 8.640 (dd, 1H, $^4\text{J}_{\text{H2'-H4'}} = 2.1$ Hz, $^4\text{J}_{\text{H2'-H6'}} = 1.8$ Hz, 2'-H) |
| 5c | 6.517 (d, 1H, $^3\text{J}_{\text{H4-H3}} = 1.9$ Hz, 4-H), 7.612-7.934 (m, 4H, ArH ₄), 8.351 (d, 1H, $^3\text{J}_{\text{H3-H4}} = 1.9$ Hz, 3-H) |
| 6a | 8.338 (m AA'BB', 4H, ArH ₄), 8.963 (s, 1H, 3-H) |
| 6b | 7.823 (dd, 1H, $^3\text{J}_{\text{H5'-H4'}} = 8.3$ Hz, $^3\text{J}_{\text{H5'-H6'}} = 8.0$ Hz, 5'-H), 8.375 (ddd, 1H, $^3\text{J}_{\text{H6'-H5'}} = 8.0$ Hz, $^4\text{J}_{\text{H6'-H2'}} = 1.8$ Hz, $^4\text{J}_{\text{H6'-H4'}} = 1.0$ Hz, 6'-H), 8.515 (ddd, 1H, $^3\text{J}_{\text{H4'-H5'}} = 8.3$ Hz, $^4\text{J}_{\text{H4'-H2'}} = 2.1$ Hz, $^4\text{J}_{\text{H4'-H6'}} = 1.0$ Hz, 4'-H), 8.920 (dd, 1H, $^4\text{J}_{\text{H2'-H4'}} = 2.1$ Hz, $^4\text{J}_{\text{H2'-H6'}} = 1.8$ Hz, 2'-H), 8.966 (s, 1H, 3-H) |
| 7a | 2.401 (s, 3H, 3-Me), 6.557 (s, 1H, 4-H), 8.133 (m AA'BB', 4H, ArH ₄) |
| 7b | 2.401 (s, 3H, 3-Me), 6.535 (s, 1H, 4-H), 7.668 (dd, 1H, $^3\text{J}_{\text{H5'-H4'}} = 8.1$ Hz, $^3\text{J}_{\text{H5'-H6'}} = 7.8$ Hz, 5'-H), 8.097 (ddd, 1H, $^3\text{J}_{\text{H6'-H5'}} = 7.8$ Hz, $^4\text{J}_{\text{H6'-H2'}} = 1.6$ Hz, $^4\text{J}_{\text{H6'-H4'}} = 1.1$ Hz, 6'-H), 8.279 (ddd, 1H, $^3\text{J}_{\text{H4'-H5'}} = 8.1$ Hz, $^4\text{J}_{\text{H4'-H2'}} = 2.3$ Hz, $^4\text{J}_{\text{H4'-H6'}} = 1.1$ Hz, 4'-H), 8.588 (dd, 1H, $^4\text{J}_{\text{H2'-H4'}} = 2.3$ Hz, $^4\text{J}_{\text{H2'-H6'}} = 1.6$ Hz, 2'-H) |
| 7c | 2.401 (s, 3H, 3-Me), 6.337 (s, 1H, 4-H), 7.578-7.892 (m, 4H, ArH ₄) |
| 9 | 2.600 (s, 3H, 3-Me), 9.229 (s, 1H, 5-H) |
| 10 | 2.859 (d, 3H, $^5\text{J}_{\text{Me-H3}} = 0.6$ Hz, 5-Me), 8.743 (q, 1H, $^5\text{J}_{\text{H3-Me}} = 0.6$ Hz, 3-H) |
| 11 | 2.534 (s, 3H, 3-Me), 2.800 (s, 3H, 5-Me) |

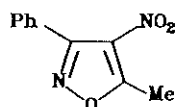
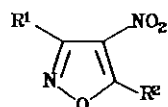
In the light of these findings and bearing in mind the possibility of achieving a preferential nitration at position 4 for 3-phenyl-⁹ and 3,5-diphenylisoxazoles¹⁰ with $\text{Ac}_2\text{O-HNO}_3$, we investigated the possibility of obtaining 3 and 4

by this route. Thus, when the isoxazole **1** was allowed to react with nitric acid in acetic anhydride for 70 h at 5-10 °C, we obtained, besides some unreacted material and a mixture of the nitrophenyl derivatives **5a-c**, the desired compound **3** as the major component, whose structure follows from spectral evidence. In fact, as for compounds **6a,b**, the lack of any signal attributable to H-4 and the appearance of a weak resonance at δ 129.90 ppm (C-NO₂) in the ¹H- and ¹³C-nmr spectra, respectively, together with the presence of a mono substituted phenyl ring (¹H-,

Table 2. ¹³C-nmr data

| Compound | ¹³ C-nmr (δ , ppm, CDCl ₃) |
|-----------|--|
| 1 | 98.51 (d, C-4, ¹ J _{C4-H4} = 181.6 Hz, ² J _{C4-H3} = 9.45 Hz), 125.615 (d, C _{meta}), 127.01 (s, C _{ipso}), 128.79 (d, C _{ortho}), 129.98 (d, C _{para}), 150.64 (d, C-3, ¹ J _{C3-H3} = 186.1 Hz, ² J _{C3-H4} = 5.5 Hz), 169.09 (s, C-5) |
| 2 | 11.46 (q, Me-3, ¹ J _{Me} = 129.5 Hz), 100.07 (d, C-4, ¹ J _{C4-H4} = 178.95 Hz, ³ J _{C4-Me} = 3.2 Hz), 125.64 (d, C _{meta}), 127.47 (s, C _{ipso}), 128.83 (d, C _{ortho}), 129.89 (d, C _{para}), 160.27 (s, C-3), 169.51 (s, C-5) |
| 3 | 123.97 (s, C _{ipso}), 128.91 (d, C _{ortho}), 129.59 (d, C _{meta}), 129.90 (s, C-4), 133.095 (d, C _{para}), 147.75 (d, C-3, ¹ J _{C3-H3} = 197.4 Hz), 167.54 (s, C-5) |
| 4 | 11.90 (q, Me-3, ¹ J _{Me} = 131.9 Hz), 124.70 (s, C _{ipso}), 128.66 (d, C _{ortho}), 129.00 (s, C-4), 129.25 (d, C _{meta}), 132.54 (d, C _{para}), 156.62 (s, C-3, ² J _{C3-Me} = 7.1 Hz), 168.65 (s, C-5) |
| 5a | 101.36 (d, C-4, ¹ J _{C4-H4} = 182.4 Hz, ² J _{C4-H3} = 9.4 Hz), 124.47 (d, C-2',6'/C-3',5'), 126.67 (d, C-3',5'/C-2',6'), 132.62 (s, C-1'), 148.495 (s, C-4'), 151.13 (d, C-3, ¹ J _{C3-H3} = 188.0 Hz, ² J _{C3-H4} = 5.2 Hz), 166.86 (s, C-5) |
| 6a | 124.01 (d, C-2',6'/C-3',5'), 129.38 (s, C-1'), 130.86 (d, C-3',5'/C-2',6'), 131.04 (s, C-4), 147.79 (d, C-3, ¹ J _{C3-H3} = 198.7 Hz), 150.08 (s, C-4'), 165.00 (s, C-5) |
| 6b | 124.75 (d, C-5', ¹ J _{C5'-H5'} = 171.8 Hz, ² J _{C5'-H4'} = ² J _{C5'-H6'} = 5 Hz), 125.44 (s, C-1'), 127.38 (d, C-6'/C-4', ¹ J = 170.0 Hz, ² J = 7.9 Hz, ³ J = 1.7 Hz), 130.275 (d, C-2', ¹ J _{C2'-H2'} = 167.8 Hz), 130.77 (s, C-4), 135.10 (d, C-4'/C-6', ¹ J = 167.0 Hz, ² J = 4.0 Hz, ³ J = 2.0 Hz), 147.79 (d, C-3, ¹ J _{C3-H3} = 198.7 Hz), 148.36 (s, C-3'), 164.89 (s, C-5) |
| 7a | 11.60 (q, Me-3, ¹ J _{Me} = 129.5 Hz), 102.84 (d, C-4, ¹ J _{C4-H4} = 179.8 Hz, ³ J _{C4-Me} = 3.1 Hz), 124.38 (d, C-2',6'/C-3',5'), 126.49 (d, C-3',5'/C-2',6'), 132.98 (s, C-1'), 148.35 (s, C-4'), 160.78 (s, C-3, ² J _{C3-Me} = 6.7 Hz, ² J _{C3-H4} = 4.95 Hz), 167.08 (s, C-5) |
| 9 | 10.57 (q, Me-3, ¹ J _{Me} = 132.2 Hz), 134.54 (s, C-4), 154.45 (s, C-3, ² J _{C3-Me} = 7.1 Hz, ³ J _{C3-H5} = 4.5 Hz), 159.465 (d, C-5, ¹ J _{C5-H5} = 211.7 Hz) |
| 10 | 12.93 (q, Me-5, ¹ J _{Me} = 132.8 Hz), 131.03 (s, C-4), 145.84 (d, C-3, ¹ J _{C3-H3} = 197.9 Hz), 170.64 (s, C-5, ² J _{C5-Me} = 7.2 Hz, ³ J _{C5-H3} = 2.8 Hz) |
| 11 | 11.46 (q, Me-3, ¹ J _{Me} = 131.8 Hz), 13.775 (q, Me-5, ¹ J _{Me} = 132.5 Hz), 130.07 (s, C-4), 155.475 (s, C-3, ² J _{C3-Me} = 7.2 Hz), 171.87 (s, C-5, ² J _{C5-Me} = 7.2 Hz) |

^{13}C -nmr, and mass spectra) and a nitro group (mass spectrum), unambiguously confirm the assigned structure. The same procedure applied to compound **2** to give 3-methyl-4-nitro-5-phenylisoxazole (**4**) as the largely predominant product, together with compounds **7a-c**. Compound **4** was previously reported by Russian workers¹¹ as the reaction product of 3-bromo-1-phenyl-1-butyne with sodium nitrite in DMF, but more recently Duranti and coworkers¹² unambiguously established the nature of this compound as the isomeric 5-methyl-4-nitro-3-phenylisoxazole (**8**). The physical properties of our product are sensibly different with respect to those reported for **8**; in particular, a careful comparison of its ^1H -nmr spectrum with those of **8** and well established model compounds (see below) allowed us to state that the chemical shift of the methyl group is indicative of its position on the 4-nitroisoxazole ring. Thus, the methyl resonance of compound **4** (2.635 ppm) is very close to that of 3-methyl-4-nitroisoxazole (**9**)¹³ (2.602 ppm), whereas the reported value for the regioisomer (**8**) (2.85 ppm),^{11,12} is identical with that of 5-methyl-4-nitroisoxazole (**10**)¹³ (2.859 ppm).

**8****9** $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$ **10** $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ **11** $\text{R}^1 = \text{R}^2 = \text{Me}$

Finally, 3,5-dimethyl-4-nitroisoxazole (**11**) exhibits two resonances at δ 2.801 and 2.511 ppm which are easily assigned to methyl groups at positions 5 and 3, respectively, by selective heteronuclear decouplings or by a 2D-nmr (HETCOR) experiment, thus confirming the above statement.

EXPERIMENTAL

All melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra were measured for potassium bromide discs with a Perkin-Elmer 283 spectrophotometer. ^1H - and ^{13}C -nmr spectra were recorded in CDCl_3 on a Varian VXR-300 instrument; chemical shifts are reported in ppm high frequency from tetramethylsilane as secondary reference standard and coupling constants in Hz. Mass spectra were obtained with a Hewlett-Packard 5790A instrument. Silica gel plates (Merck F₂₅₄) and silica gel 60 (Merck 230-400 mesh) were used for analytical tlc and for flash chromatographies, respectively. Solvents were removed under reduced pressure.

Nitration of Compounds 1 and 2 with HNO₃-H₂SO₄

a) 5-Phenylisoxazole **1** (1.6 g; 11.03 mmol) was dissolved dropwise in H₂SO₄ (5.4 ml; d = 1.84 g/l) at -10 °C, with stirring to minimize local overheating. A mixture of HNO₃ (2.4 ml; d = 1.49 g/l) in H₂SO₄ (3.6 ml; d = 1.84 g/l) was then added dropwise, the temperature being held between -5 and -2 °C. After addition was complete, the mixture was maintained for 1 h at 15-18 °C, then carefully poured into ice and filtered to give a solid (1.848 g) which was washed with water and dried. The raw material showing three spots in tlc was resolved by flash chromatography with ethyl acetate-petroleum ether (bp 40-70 °C) (1:4 v/v) as eluant. The fastest running band afforded compound **6a** (0.150 g, yield 6%), mp 119-120 °C (from methanol) [lit.² mp 115-117 °C (from ethanol)]. Ms: m/z (%) = 235 (39) [M⁺], 166 (75), 150 (100), 120 (24), 104 (63), 92 (47), and 76 (85). Anal. Calcd for C₉H₅N₃O₅: C, 45.97; H, 2.14; N, 17.87. Found: C, 45.82; H, 2.23; N, 17.68.

The second band afforded a small amount of compound **6b** (0.120 g, yield 5%), mp 104-106 °C (from methanol). Ms: m/z (%) = 235 (29) [M⁺], 166 (70), 150 (100), 104 (51), 92 (18), and 76 (68). Anal. Calcd for C₉H₅N₃O₅: C, 45.97; H, 2.14; N, 17.87. Found: C, 45.74; H, 2.27; N, 17.71.

The slowest component was identified (¹H- and ¹³C-nmr) as a mixture of the three mononitrophenyl derivatives **5a-c**, (1.2 g, yield 57%). Fractional crystallizations from methanol gave pure compound **5a**, mp 167-168 °C (lit.¹ mp 171-172 °C, lit.² mp 176-178 °C, lit.³ mp 163-165 °C). Ms: m/z (%) = 190 (100) [M⁺], 150 (40), 144 (10), 104 (22), 76 (26), and 68 (9). Anal. Calcd for C₉H₆N₂O₃: C, 56.85; H, 3.18; N, 14.73. Found: C, 56.70; H, 3.09; N, 14.82.

b) Operating as described above, compound **2** (0.666 g; 4.19 mmol) afforded a white solid (0.795 g, yield 93%) containing the isomers **7a-c** (ca. 2:1:0.5, ¹H-nmr spectrum) which showed the same R_f and retention times in different eluants or chromatographic columns, respectively. Fractional crystallizations from ethanol gave an analytical sample of 3-methyl-5-*p*-nitrophenylisoxazole (**7a**), mp 180-181 °C (lit.¹⁴ 180 °C, lit.⁴ 183-185 °C) and enriched (ca. 90%) samples of **7b** and **7c**. Anal. Calcd for C₁₀H₈N₂O₃: C, 58.82; H, 3.95; N, 13.72. Found: C, 58.96; H, 3.78; N, 13.56.

Nitration of Compounds 1 and 2 with HNO₃ in acetic anhydride

a) A solution of 5-phenylisoxazole **1** (0.63 g; 4.34 mmol) in acetic anhydride (2.2 ml) was cooled to 0 °C and HNO₃ (0.43 ml; d = 1.49 g/l) was added dropwise under stirring, the temperature being maintained between 0-

5 °C. After addition was complete, the mixture was stirred for 70 h at 5-10 °C and then poured into ice to give a gummy solid which was extracted with methylene chloride (4 x 40 ml). Evaporation to dryness of the extracts left a yellowish residue which was resolved into three components by flash chromatography with ethyl acetate-petroleum ether (bp 40-70 °C) (1:4 v/v) as eluant. The fastest band gave 4-nitro-5-phenylisoxazole (**3**) (0.185 g, yield 32%), mp 87-88 °C after crystallization from ethanol. Ms: m/z (%) = 190 (44) [M⁺], 121 (86), 105 (41), 93(27), and 77 (100). *Anal.* Calcd for C₉H₆N₂O₃: C, 56.85; H, 3.18; N, 14.73. Found: C, 56.61; H, 3.12; N, 14.94. The second compound was easily recognized (¹H- and ¹³C-nmr) as unreacted 5-phenylisoxazole (0.190 g), whereas the slowest band afforded a solid (0.166 g, yield 29%) containing the isomers **5a** and **5c** as predominant products together with a small amount of the *m*-nitrophenyl derivative **5b** (¹H-nmr spectrum).

b) Operating under the same conditions, compound **2** (1 g; 6.29 mmol) afforded a yellow oily product which was extracted with methylene chloride (3 x 40 ml) and resolved into three components by flash chromatography with ethyl acetate-petroleum ether (bp 40-70 °C) (1:4 v/v). The first band afforded 3-methyl-4-nitro-5-phenylisoxazole (**4**) (0.63 g, yield 59%) as a yellow oil which solidifies on cooling, mp 31-32 °C (from methanol). *Anal.* Calcd for C₁₀H₈N₂O₃: C, 58.82; H, 3.95; N, 13.72. Found: C, 59.01; H, 4.01; N, 13.66.

The second compound was identified (¹H-nmr) as unreacted starting material (0.170 g), whereas the third band gave a solid (0.2 g, yield 19%) containing almost exclusively (¹H-nmr spectrum) compound **7a** together with small amounts of the regioisomers **7b** and **7c**.

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