**N-Isocyanoiomines. Preparation and Characterisation**

PALLE JAKOBSEN

Medicinsk-Kemisk Institut, University of Copenhagen, Rådmandsgade 71, DK-2200 Copenhagen, Denmark

Aromatic N-isocyanoiomines have been reported as intermediates in the synthesis of formhydrazonoesters. In a few cases the N-isocyanoiomines have been isolated, but comments on yield and reactivity are sparse. Aliphatic N-isocyanoiomines have not been described.

This paper reports the synthesis of aliphatic N-isocyanoiomines. The hitherto unknown compounds were characterized by their α-addition products from reactions with piperidine and with ethanethiol.

N-Isocyanoiomines (I) were synthesized by two different methods: dehydration of N'-alkylidene formohydrazides by means of POCl₃ and triethylamine in CH₂Cl₂-solution (method A), and reaction between hydrazones and CHCl₃ in NaOH-solution, with use of benzyltriyethylammonium chloride as phase transfer catalyst (Method B).

\[
\text{RR'C = N-NHCHO + POCl₃ + Et₃N} \\
\text{RR'C = N-NH₂ + CHCl₃ + OH⁻} \\
\]

**Scheme 1.** (Compound, R, R'): (a, Me, Me), (b, Et, Et), (c, Pr', Pr'), (d, Me, Ph), (e, Ph, Ph).

Attempts to purify N-isocyanoiomines by distillation in vacuo resulted in products contaminated with triethylamine. The distillate was collected in an acetone/dry ice trap. The compounds (I) decomposed rapidly at room temperature, whereas they were stable for some days in solution. All formed N-isocyanoiomines showed strong, sharp IR absorptions around 2100 cm⁻¹, and had the characteristic isocyanide smell. The use of pyridine in the dehydrating step instead of triethylamine gave no N-isocyanoiomine.

For further characterisation of 1α-δ the CH₂Cl₂-phase from the reaction mixture was used. The reaction with piperidine, catalysed by CuCl₂, was found to be convenient for trapping the N-isocyanoiomines, as it took about 2 h at room temperature, giving formamidrazone in overall yields from 11 to 38%. The analogous reaction for t-butyl isocyanide proceeds in 10 h at room temperature.

\[
\text{RR'C = N-N = C + HN(CH₃)₂} \\
\text{1α-δ} \\
\text{RR'C = N-N = CH-N(CH₃)₂} \\
\text{2α-δ} \\
\]

**Scheme 2.**

\[
(\text{Et₂})₄N = N-N = C + \text{EtSH} \rightarrow \text{δb} \\
(\text{Et₂})₄C = N-N = \text{Et-S-CH}_3 \rightarrow \text{3b} \\
\]

**Scheme 3.**

\[\text{N'-[(3-Pentylidene) formohydradide and N'-(1-phenylethylidene) formodyhydradide were prepared as described for N'-[2-propylidene] formohydradide,} \]

\[\text{Yield 89%, m.p. 73-74°C. Anal. C₉H₁₄N₂O: C, H, N. N'-[(1-Phenylethylidene) formohydradide.} \]

\[\text{Yield 60%, m.p. 157-158°C. Anal. C₉H₁₄N₂O: C, H, N. N'-[2,4-Dimethyl-[3-pentylidene] formohydradide was prepared by refluxing 2,4-dimethyl-3-pentanone hydradone (0.19 mol) in ethyl formate (60 ml) for 6 h. After subsequent stirring at room temperature for 10 days, the mixture was evaporated to dryness and the resulting product was recrystallized from ethanol. M.p. 113°C, yield 55%. Anal. C₉H₁₄N₂O: C, H, N.} \]

\[\text{N'-[3-Propylidene] formohydradide (19). N'-[2-Propylidene] formohydradide (0.1 mol) and triethylamine (60 ml) were dissolved in CH₂Cl₂ (50 ml). POCl₃ (9.3 g) was added dropwise under cooling with ice. The temperature was 42-45°C. The resulting mixture was stirred at room temperature for 3 h. Saturated Na₂CO₃ solution (70 ml) was added under cooling, the CH₂Cl₂-layer separated, dried over K₂CO₃, and used for further reactions.} \]

An attempt to isolate the N-isocyanoinime by distillation of a CH₂Cl₂-layer evaporated previously to ca. 30 ml gave 1.5 g of a liquid, b.p. 15–20 °C/1 mmHg. The distillate was cooled in dry ice/acetonc. IR absorption (CH₂Cl₂): NC 2100 cm⁻¹. On heating to room temperature the liquid decomposed rapidly, with a colour change from light yellow to dark brown. In CH₂Cl₂ or CCl₄-solution, the decomposition proceeded slower; there was still an NC IR absorption in CCl₄-solution after 7 h at room temperature. ¹H NMR spectra showed that the distillate was a mixture of triethylamine and N-isocyanoinime.

N⁴-Pentamethylene-N³-(2-propyldiene) formamidine hydrazone (2a). The CH₂Cl₂-phase described above was mixed with piperidine (0.1 mol) and CuCl (100 mg). After stirring for 2 h at room temperature the mixture was filtered and the residue distilled in vacuo. B.p. 63–84 °C/0.1 mmHg, yield 22 %. Anal. C₉H₆N₂C₂ H. N. ¹H NMR (CDCl₃): δ 7.86 (1 H, s), 3.1–3.5 (4 H, m), 2.02 (3 H, s), 1.95 (3 H, s), 1.33–1.75 (6 H, m). MS m/e (% of base peak): 167(57)M⁺, 152(5), 111(11), 84(74), 83(100), 58(13), 56(24), 55(40), 42(35), 41(30).

N⁴-Isocyno-3-pentanitiane (1b) was prepared in CH₂Cl₂/Et₂N-solution as described for (1a). Evaporation in vacuo to a volume of ca. 30 ml followed by distillation in vacuo, gave 2.4 g of a mixture of N-isocynoinimoine (1b) and triethylamine b.p. 14–16 °C/0.5 mmHg. IR absorption (CH₂Cl₂): NC 2100 cm⁻¹.

N⁴-Pentamethylene-N³-(3-pentyldiene) formamidine hydrazone (2b) was prepared analogously to 2a. B.p. 75 °C/0.05 mmHg, yield 38 %. Anal. C₁₅H₁₂N₂C₁₂ H. N. ¹H NMR (CDCl₃): δ 7.82 (1 H, s), 3.2–3.5 (4 H, m), 2.51 (2 H, q), 2.25 (2 H, q), 1.5–1.7 (6 H, m) 1.11 (3 H, t), 1.07 (3 H, t). MS m/e (% of base peak): 196(14), 195(64)M⁺, 166(13), 111(53), 86(27), 84(100), 83(91), 69(11), 56(34), 55(34), 42(10), 41(27).

N⁴-(2,4-Dimethyl-3-pentynitile)-N³-pentamethyleneformamidine hydrazone (2c) was prepared from N-isocyano-2,4-dimethyl-3-pentynitile (Method A) as described for 2a, yield 39 %, b.p. 78–80 °C/0.02 mmHg. Anal. C₁₅H₁₂N₂C₁₂ H. N. ¹H NMR (CDCl₃): δ 7.78 (1 H, s), 3.51 (1 H, sep.), 3.48–3.19 (4 H, m), 2.58 (1 H, sep.), 1.55–1.65 (6 H, m), 1.17 (6 H, s), 1.06 (6 H, s). MS m/e (% of base peak): 224(11), 223(50)M⁺, 180(16), 139(22), 114(11), 113(11), 112(15), 111(27), 85(9), 84(100), 83(42), 70(13), 69(16), 56(13), 55(31), 42(23), 42(27), 41(37).

N⁴-Isoocyano-2,4-dimethyl-3-pentynitile (1c). (Method B). A mixture of diisopropyl ketone hydrazone ⁴ (0.1 mol), chloroform (0.1 mol), aqueous NaOH-solution (50 mol, 50 %), benzyltritylammonium chloride (0.5 g) and CH₂Cl₂ (50 ml) was stirred at room temperature for 2.5 h (slightly exothermic reaction). The CH₂Cl₂-layer was separated and dried over K₂CO₃. IR (CH₂Cl₂): NC 2095 cm⁻¹. The N-isocyanoimine could be stored for a few days in solution, with slight decomposition. Subsequent treatment with piperidine and CuCl as described for 1a gave 11 % of 2c.

N⁴-Isoocyano-1-phenylethanimine (1d). Preparation by Method B gave mainly acetophenone azine. Method A gave the N-isocyanoinime in solution, IR (CH₂Cl₂): NC 2090 cm⁻¹.

N⁴-Pentamethylene-N³-(1-phenylethylidene) formamidine hydrazone (2d). Prepared analogous to 2a. B.p. 138–140 °C/0.05 mmHg, m.p. 43 °C (EtOH), yield 30 %. Anal. C₁₅H₁₆N₂C₂ H. N. ¹H NMR (CDCl₃): δ 8.05 (1 H, s), 7.2–7.8 (5 H, m), 3.2–3.6 (4 H, m), 2.42 (3 H, s), 1.5–1.7 (6 H, m). MS m/e (% of base peak): (azine contaminated) 230(15), 229(70)M⁺, 217(62), 145(15), 120(85), 119(15), 118(17), 111(23), 110(13), 104(32), 103(36), 99(21), 97(25), 85(10), 84(77), 83(100), 77(60), 72(51), 71(32), 58(13), 57(13), 56(47), 55(38), 51(27), 50(12), 44(49), 43(16), 42(38), 41(34), 40(9).

N⁴-Isocyano-3-phenyldiphenylmethanimine (1e). Benzophenonehydrazone (0.1 mol), CH₂Cl₂ (0.1 mol), NaOH-solution (50 ml, 50 %) and benzyltritylammonium chloride (0.5 g) were stirred in 50 ml CH₂Cl₂ for 5 days at room temperature. The CH₂Cl₂-layer was separated and dried over K₂CO₃, IR (CH₂Cl₂): NC 2060 cm⁻¹. After treatment with piperidine no formamidine hydrazone was isolated.

S-Ethyl-N³-(3-pentyldiene) thioformyldrazoate (3b). N-Isoocyano-3-pentynitile in CH₂Cl₂/Et₂N-solution, ethanethiol (0.5 mol) and CuCl (0.5 mmol) were stirred at room temperature for 1 h. The solvent was evaporated and the residue distilled in vacuo, b.p. 46 °C/0.1 mmHg, yield 19 %. ¹H NMR (CDCl₃): δ 8.25 and 7.65 (1 H, singlets, intensity 1/3), 3.1–2.1 (6 H, 3 quartets), 1.5–0.8 (9 H, 3 triplets). MS m/e (% of base peak): 172(32)M⁺, 143(14), 139(13), 111(25), 88(42), 86(21), 84(10), 61(25), 60(13), 56(100), 55(10), 54(19), 45(11), 41(17).


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