



An attempt to isolate the *N*-isocyanimine by distillation of a  $\text{CH}_2\text{Cl}_2$ -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/acetone. IR absorption ( $\text{CH}_2\text{Cl}_2$ ): NC 2100  $\text{cm}^{-1}$ . On heating to room temperature the liquid decomposed rapidly, with a colour change from light yellow to dark brown. In  $\text{CH}_2\text{Cl}_2$  or  $\text{CCl}_4$ -solution, the decomposition proceeded slower; there was still an NC IR absorption in  $\text{CCl}_4$ -solution after 7 h at room temperature.  $^1\text{H}$  NMR spectra showed that the distillate was a mixture of triethylamine and *N*-isocyanimine.

*N*<sup>1</sup>-Pentamethylene-*N*<sup>3</sup>-(2-propylidene) formamide hydrazone (2a). The  $\text{CH}_2\text{Cl}_2$ -phase described above was mixed with piperidine (0.1 mol) and  $\text{CuCl}$  (100 mg). After stirring for 2 h at room temperature the mixture was filtered and the filtrate distilled *in vacuo*. B.p. 63–64 °C/0.1 mmHg, yield 2%. Anal.  $\text{C}_9\text{H}_{17}\text{N}_3$ : C, H, N.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 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) $\text{M}^+$ , 152(5), 111(11), 84(74), 83(100), 58(13), 56(24), 55(40), 42(35), 41(30).

*N*-Isocyanato-3-pentanimine (1b) was prepared in  $\text{CH}_2\text{Cl}_2/\text{Et}_3\text{N}$ -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*-isocyanimine (1b) and triethylamine b.p. 14–18 °C/0.5 mmHg. IR absorption ( $\text{CH}_2\text{Cl}_2$ ): NC 2100  $\text{cm}^{-1}$ .

*N*<sup>1</sup>-Pentamethylene-*N*<sup>3</sup>-(3-pentylidene) formamide hydrazone (2b) was prepared analogous to 2a. B.p. 75 °C/0.05 mmHg, yield 38%. Anal.  $\text{C}_{11}\text{H}_{21}\text{N}_3$ : C, H, N.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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) $\text{M}^+$ , 166(13), 111(53), 86(27), 84(100), 83(91), 69(11), 56(34), 55(34), 42(10), 41(27).

*N*<sup>3</sup>-(2,4-Dimethyl-3-pentylidene) *N*<sup>1</sup>-pentamethyleneformamide hydrazone (2c) was prepared from *N*-isocyanato-2,4-dimethyl-3-pentanimine (Method A) as described for 2a, yield 36%, b.p. 78–80 °C/0.02 mmHg. Anal.  $\text{C}_{13}\text{H}_{25}\text{N}_3$ : C, H, N.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.76 (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) $\text{M}^+$ , 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).

*N*-Isocyanato-2,4-dimethyl-3-pentanimine (1c). (Method B). A mixture of diisopropyl ketone hydrazone<sup>8</sup> (0.1 mol), chloroform (0.1 mol), aqueous NaOH-solution (50 ml, 50%), benzyltriethylammonium chloride (0.5 g) and  $\text{CH}_2\text{Cl}_2$  (50 ml) was stirred at room temperature for 2.5 h (slightly exothermic reaction). The  $\text{CH}_2\text{Cl}_2$ -layer was separated and dried over  $\text{K}_2\text{CO}_3$ . IR ( $\text{CH}_2\text{Cl}_2$ ): NC 2095  $\text{cm}^{-1}$ . The *N*-isocyanimine could be stored for a few days

in solution, with slight decomposition. Subsequent treatment with piperidine and  $\text{CuCl}$  as described for 1a gave 11% of 2c.

*N*-Isocyanato-1-phenylethanimine (1d). Preparation by Method B gave mainly acetophenone azine. Method A gave the *N*-isocyanimine in solution, IR ( $\text{CH}_2\text{Cl}_2$ ): NC 2090  $\text{cm}^{-1}$ .

*N*<sup>1</sup>-Pentamethylene-*N*<sup>3</sup>-(1-phenylethylidene) formamide hydrazone (2d). Prepared analogous to 2a. B.p. 138–140 °C/0.05 mmHg, m.p. 43 °C ( $\text{EtOH}$ ), yield 30%. Anal.  $\text{C}_{14}\text{H}_{19}\text{N}_3$ : C, H, N.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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) $\text{M}^+$ , 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(40), 43(15), 42(38), 41(34), 40(9).

*N*-Isocyanodiphenylmethanimine (1e). Benzophenonehydrazone (0.1 mol),  $\text{CHCl}_3$  (0.1 mol), NaOH-solution (50 ml, 50%) and benzyltriethylammonium chloride (0.5 g) were stirred in 50 ml  $\text{CH}_2\text{Cl}_2$  for 5 days at room temperature. The  $\text{CH}_2\text{Cl}_2$ -layer was separated and dried over  $\text{K}_2\text{CO}_3$ . IR ( $\text{CH}_2\text{Cl}_2$ ): NC 2060  $\text{cm}^{-1}$ . After treatment with piperidine no formamide hydrazone was isolated.

*S*-Ethyl-*N*-(3-pentylidene) thioformhydrazone (3b). *N*-Isocyanato-3-pentanimine in  $\text{CH}_2\text{Cl}_2/\text{Et}_3\text{N}$ -solution, ethanethiol (0.5 mol) and  $\text{CuCl}$  (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%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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) $\text{M}^+$ , 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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