

IR spectra were recorded on a Hitachi Model EPI-G3 and ^1H NMR spectra on a JEOL JNM 4H 100 spectrometer.

Mass spectra were obtained by JEOL JMC OISG-2 spectrometer.

Commercially available morpholine and 4-methylmorpholine were used after distillation. Ethyl azidoformate was prepared according to the method of Lwowski and Mattingly.⁷⁾

Authentic 4-(ethoxycarbonyl)morpholine was prepared from morpholine and ethyl chloroformate by usual procedures.⁷⁾

Reaction of Ethyl Azidoformate (1) with Morpholine (2). The azide **1** (2.0 g; 0.017 mol) was added at room temperature to **2** (7.5 g; 0.087 mol) with stirring. During the addition, a white solid rapidly separated without any evolution of gases. The mixture was then heated to 120 °C and kept at that temperature for 2 h. After cooling to room temperature the resulting solid was separated on a filter, washed with ether, dried *in vacuo* and recrystallized from hot methanol to give **4** as white needles, mp 129.2–130.2 °C (yield; 1.89 g; 86.1%). Soluble in water but insoluble in ether and benzene. IR (KBr) 2450 (NH_2^+), 2030 (N_3^-) and 1590 cm^{-1} (NH_2^+); ^1H NMR ($(\text{CD}_3)_2\text{SO}$) δ =3.15 (4H, m, N-CH₂), 3.8 (4H, m, O-CH₂) and 7.35 (2H, br, NH₂, disappeared by treatment with D₂O); MS *m/e*: 87 (M–HN₃) and 43 (HN₃); Found: C, 36.82; H, 7.58; N, 43.20%. Calcd for C₄H₁₀ON₄: C, 36.91; H, 7.74; N, 43.50%.

The filtrate was fractionally distilled *in vacuo* to give **5** (yield; 1.53 g; 57%): bp 111.2 °C/25 mmHg: IR (neat) 2950 (–CH₃), 1700 (C=O) and 1240 cm^{-1} (=C–O–C); ^1H NMR (CCl₄) δ =1.29 (3H, t, CH₃–), 3.36–3.8 (8H, m, ring proton) and 4.1 (2H, q, –CH₂–); MS *m/e*: 159 (M); Found: C, 52.60; H, 8.49; N, 8.61%. Calcd for C₇H₁₃O₃N: C, 52.82; H, 8.23; N, 8.80%. IR spectrum of **5** was identical in all respects with that of an authentic sample.

Thermolysis of 1 in 4-Methylmorpholine (3). A stirred solution of **1** (2.3 g; 0.02 mol) in **3** (10.1 g; 0.1 mol) was heated to 115 °C and kept at this temperature for 3 h during which time nitrogen was smoothly evolved. After the nitrogen evolution has ceased, removal of the excess **3** from the reaction mixture *in vacuo* left a residual oil (4.2 g). The residual oil was subjected to preparative VPC on a column (8 mm×2 m) packed with 5% Silicone OV-22 on 60/80 Uniport KS (oven temperature, initial: 110 °C, final: 230 °C, rate: 10 °C/min) to separate four components. Among them, three major components were identified as ethyl car-

bamate (**6**), 4-(ethoxycarbonylamino)morpholine (**7**) and 4-methyl-3-(ethoxycarbonylamino)morpholine (**8**), respectively. The product **6** was characterized by comparison of its VPC retention time and IR spectra with those of the authentic sample. The structural assignment of the components **7** and **8** was performed on the basis of their IR, ^1H NMR and mass spectral data. Analytical data for **7**: IR (neat) 3400 (NH), 1720 (C=O) and 1250 cm^{-1} (=C–O–C); ^1H NMR (CDCl₃) δ =1.28 (3H, t, CH₃–), 2.05–3.08 (2H, m, N–CH₂), 3.5 (4H, m, H₂C–N–CH₂), 3.71 (4H, m, H₂C–O–CH₂) and 4.2 (2H, q, –CH₂–); MS *m/e* (rel intensity): 159 (M–C₂H₅ 24.1), 115 (M–CO₂C₂H₅ 7.4), 100 (M–NHCO₂C₂H₅ 29.2) and 86 (M–CH₂NHCO₂C₂H₅ 30.7). Analytical data for **8**: IR (neat) 3325 (NH), 2800 (N–CH₃) and 1710 cm^{-1} (C=O); ^1H NMR (CDCl₃) δ =1.25 (3H, t, CH₃–), 2.3 (3H, s, N–CH₃), 2.4–2.9 (3H, m, HC–N–CH₂), 3.3–3.85 (4H, m, H₂C–O–CH₂), 4.12 (2H, q, –CH₂) and 5.6 (1H, br, –NH–); MS *m/e* (rel intensity): 188 (M 45.5), 173 (M–CH₃ 5.4), 159 (M–C₂H₅ 69.7), 115 (M–CO₂C₂H₅ 17.2) and 100 (M–NHCO₂C₂H₅ 72.9).

The fourth component collected by preparative VPC was failed in its structural determination, although ^1H NMR spectra showed no peaks assignable to CH₃–, CH₂– or CH– adjacent to N.

References

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