1-Benzyl-4-formylpiperazine (III).—A mixture of 357 g. (2.03 moles) of 1-benzylpiperazine and 1218 g. (20.3 moles) of methyl formate was heated in a 3-liter rocker type bomb for 1.5 hours at 100–110°. After cooling the solution was fractionated and 393.3 g. (95%) of a thick oil obtained which solidified on standing, b.p. 166–169° (0.5 mm.), n^{27}_{D} 1.5533, m.p. 61–62°.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 70.85; H, 7.90; N, 13.72. Found: C, 70.48; H, 7.92; N, 13.79.

In a similar manner 1-formyl-4-(4-methoxybenzyl)-piperazine was prepared in 92% yield, b.p. 183–189° (1.5 mm.), n^{26}_{D} 1.5559. This product also solidified on standing, m.p. 54–56°.

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: N, 11.96. Found: N, 11.96.

1-Formylpiperazine (IV).—A solution of 70 g. (0.35 mole) of 1-benzyl-4-formylpiperazine in 150 cc. of absolute ethanol was hydrogenated in the presence of 14 g. of 5% palladium-on-charcoal under a pressure of 40 p.s.i. at 55–60°. The calculated drop in pressure was reached in about four hours. A second run was carried out under the same conditions, and the two were combined and worked up as one. After removal of the catalyst and distillation to remove the solvent, the residue was distilled, b.p. 94–97° (0.5 mm.), n^{25}_{D} 1.5084. The product weighed 66.8 g. (84%).

Anal. Calcd. for $C_5H_{10}N_2O$: C, 52.62; H, 8.83; N, 24.54. Found: C, 52.53; H, 8.82; N, 24.64.

1-Carbamyl-4-formylpiperazine.—A solution of 9.5 g. (0.083 mole) of 1-formylpiperazine in 30 cc. of water was acidified (*ca.* *p*H 6) with dilute hydrochloric acid and treated with 9.3 g. (0.115 mole) of potassium cyanate. The reaction mixture was warmed on the steam-bath for 20 minutes and evaporated to dryness. The solid residue was extracted three times with boiling ethanol and the alcoholic extracts concentrated to dryness. The oily solid (10.6 g.) was recrystallized from 75 cc. of absolute alcohol and after prolonged cooling yielded 7 g. of colorless needles, m.p. 180–182°. A sample, recrystallized for analysis, melted at 185–186°.

Anal. Calcd. for $C_6H_{11}N_2O_2$: C, 45.84; H, 7.05; N, 26.73. Found: C, 45.80; H, 6.79; N, 26.71.

1-Benzenesulfonyl-4-formylpiperazine.—To 15 g. (0.085 mole) of benzenesulfonyl chloride in 100 cc. of dry benzene was added with stirring 19.4 g. (0.17 mole) of 1-formylpiperazine in 100 cc. of dry benzene. The reaction was carried out at room temperature. The mixture was filtered from amine hydrochloride and taken to dryness after which 20.6 g. of a water-insoluble solid was obtained, m.p. 140–143°. The product was recrystallized from absolute alcohol as colorless needles, m.p. 141–143°. A sample, recrystallized a second time for analysis, melted 141–142°.

Anal. Calcd. for $C_{11}H_{14}N_2O_3S$: C, 51.95; H, 5.54; N, 11.01. Found: C, 51.97; H, 5.64; N, 11.06.

1-Acetyl-4-formylpiperazine.—Ketene was passed into a mixture of 22.8 g. (0.2 mole) of 1-formylpiperazine in 200 cc. of dry benzene for one half-hour. The solvent was removed from the yellow reaction mixture and the resultant solid residue was distilled. The product boiled at 145–149° (0.5 mm.) and weighed 16.5 g.[4]

Anal. Calcd. for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.61; N, 17.93; O, 20.63. Found: C, 53.91; H, 7.41; N, 17.79; O, 21.12.

Acknowledgment.—The authors are deeply grateful to Mr. E. F. Shelberg, Chief Microanalyst, and his staff for the analyses herein.

[4] After standing the thick oil solidified and melted over a range 72–77°. It is very soluble in water.

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n-Acrylylmorpholine

BY JOHN W. LYNN

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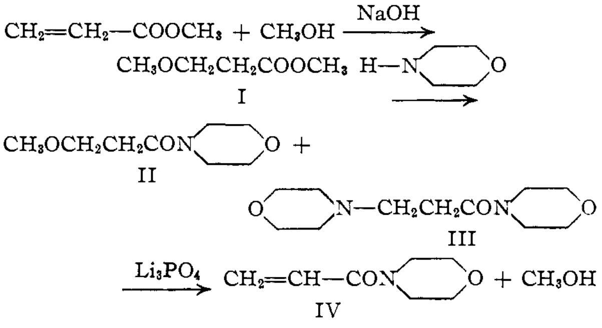
This new monomer may be obtained in substantial yield by the vapor phase dealcoholation of N-(3-methoxypropionyl)-morpholine. A recently issued patent[1] describes the syntheses of N-acrylylmorpholine by the reaction of acrylyl chloride with morpholine, but does not report any yields or physical properties.

Methyl acrylate was treated with methanol using sodium hydroxide catalyst to give methyl 3-methoxypropionate (I), which on heating with morpholine gave N-(3-methoxypropionyl)-morpholine (II) in good yield. A small amount of by-product, N-[3-(N-morpholino)-propionyl]-morpholine (III), also was obtained. Pyrolysis of the foregoing mixture in the vapor phase over lithium phosphate gave N-acrylylmorpholine (II) in about 47% yield and 65% efficiency.



Experimental[2]

Methyl 3-Methoxypropionate (I).—The procedure originally described by Purdie[3] was modified by the use of sodium hydroxide in place of sodium as catalyst. Excellent yields and efficiencies were obtained.

N-(3-Methoxypropionyl)-morpholine (II).—A mixture of 118 g. (1 mole) of methyl 3-methoxypropionate, 147 g. (2 moles) of morpholine and 18 g. (1 mole) of water was heated for 6 hours at 125° while removing 28 g. (0.87 mole) of methanol by distillation. Fractional distillation gave 144 g., an 81% yield, of N-(3-methoxypropionyl)-morpholine boiling at 127–131° (3.5 mm.) and melting at 37.5°.

Anal. Calcd. for $C_8H_{15}NO_3$: C, 55.5; H, 8.67; N, 8.09. Found: C, 55.75; H, 8.68; N, 8.33.

N-[3-(N-Morpholino)-propionyl]-morpholine (III).—A small amount of higher-melting solid was filtered from the cuts boiling higher than the products of the preceding distillation. This material proved to be the expected by-product III, melting at 91–92° of 98.8% purity by acid titration.

Anal. Calcd. for $C_{11}H_{20}N_2O_3$: C, 57.58; H, 8.78; N, 12.29. Found: C, 58.1; H, 8.82; N, 12.44.

N-Acrylylmorpholine (IV).—The method previously described by Phillips and Starcher[4] was employed for the pyrolysis step. A mixture of 342 g. (1.97 moles) of N-(3-methoxypropionyl)-morpholine, 171 g. of methanol and 2.5 g. of Agerite Powder was passed over 225 cc. of granular lithium phosphate in a 1-inch nickel tube at 390° during a 5-hour period. A slow stream of nitrogen was fed concurrently. The crude product was distilled in the presence of hydroquinone through a light-protected column. N-Acrylylmorpholine (b.p. 114–116° (8 mm.), n^{30}_{D} 1.5060, d^{20}_{20} 1.1070) was obtained in 47% yield and 65.5% efficiency.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.6; H, 7.8; N, 9.94. Found: C, 59.95; H, 8.02; N, 9.83.

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(1) G. E. Ham, U. S. Patent 2,683,703.

(2) All boiling points and melting points are uncorrected.

(3) T. Purdie and W. Marshall, *J. Chem. Soc.*, **59**, 474 (1891).

(4) B. Phillips and P. S. Starcher, U. S. Patent 2,587,209.