Anal. Calcd. for $C_{37}H_{42}N_2O_4$: C, 76.78; H, 7.32; N, 4.84. Found: C, 76.51; H, 7.36; N, 4.94.

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The Synthesis and Polymerization of N-Phenylethylenimine and the Synthesis of N,N'-Diphenylpiperazine

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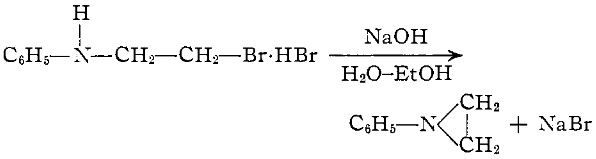
RECEIVED AUGUST 31, 1953

In the course of studies on the chemistry of ethylenimine we had occasion to synthesize N-phenylethylenimine. This compound was prepared from N-β-bromoethylaniline hydrobromide by a slight modification of the general method of Gabriel,[1] *e.g.*



Although N-phenylethylenimine is formed with considerable readiness and in 68% yield under these conditions the course of the reaction may be so altered that N,N'-diphenylpiperazine is formed as the main reaction product.

The structure of N-phenylethylenimine was established by elementary analysis and by its reaction with hydrobromic acid to form N-β-bromoethylaniline hydrobromide. An infrared analysis showed the absence of any N–H fundamental in the region of 2.9 μ, which is in accord with expectations.

N-Phenylethylenimine rapidly polymerized to a colorless solid when it was emulsified with water or was exposed to air. Polymerization also took place when N-phenylethylenimine was dissolved in methanol or ethanol and exposed to air but at a much slower rate than in water. Nitrogen analysis of the polymer gave a value corresponding to the monomer. Most likely a chain polymer was produced. The polymer was soluble in 90% formic acid and decomposed at 270–275°.

Experimental

N-Phenylethylenimine.—A solution of 115 ml. of 6 *N* sodium hydroxide and 300 ml. of 95% ethanol was placed in a one-liter three-necked flask equipped with a stirrer, condenser and dropping funnel, and the flask immersed in a water-bath held at 50°. To this was added dropwise and with stirring 84.3 g. of N-β-bromoethylaniline hydrobromide[2] dissolved in 120 ml. of water and 80 ml. of 95% ethanol. After the addition was completed the water-bath was raised to 85° for one hour. The condenser was then arranged for downward distillation and 220 ml. of ethanol was removed by distillation. The residue was cooled to room temperature and extracted with six 50-ml. portions of ether. The ethereal solution was dried over sodium sulfate, filtered and distilled until the temperature reached 82°. The residue separated into two layers at this point. The lower layer consisted of water and ethanol. The top layer was removed by means of a suction pipet, dried with sodium sulfate and subjected to vacuum distillation. A fraction of 24.3 g. (68%) boiling at 70–70.5° at 13 mm. or 60.5–61° at 9 mm. was obtained; $n^{25}\text{D}$ 1.5498, $n^{20}\text{D}$ 1.5524.

Anal. Calcd. for C_8H_9N: C, 80.5; H, 7.6; N, 11.8. Found[3]: C, 80.5; H, 7.7; N, 11.8.

The N-phenylethylenimine was converted into N-β-bromoethylaniline hydrobromide by the following procedure: 2.2 g. of N-phenylethylenimine was added quickly to 60 ml. of cold 48% hydrobromic acid. The reaction mixture was refluxed gently for one-half hour and then distilled until 50 ml. of distillate was collected. The residue was cooled in a vacuum desiccator. The crude N-β-bromoethylaniline hydrobromide crystallized on standing. Recrystallization from absolute ethanol gave a 65% yield of pure N-β-bromoethylaniline hydrobromide melting at 138–139°. A mixture of this substance with authentic N-β-bromoethylaniline hydrobromide melted at 137–140°.

Poly-N-phenylethylenimine.—Two grams of N-phenylethylenimine was shaken with 25 ml. of water. The emulsion rapidly became milky-white and a precipitate formed within an hour. This material was filtered and dried; yield 1.94 g. The polymer turned brown at 230° and gradually shriveled and melted completely at 270–275°.

Anal. Calcd. for $(C_8H_9N)_n$: N, 11.8. Found: N, 11.6.

N,N'-Diphenylpiperazine.—To 17.6 g. of N-β-bromoethylaniline hydrobromide was added a solution containing 6 g. of NaOH in 10 ml. of water. Two layers formed. Twenty ml. of water was added and the mixture heated in a water-bath at 85° for two hours. The oily layer solidified, was filtered and dried. The product was recrystallized from methanol yielding 5.0 g. (67%) of white crystals melting at 163–164°. The literature value for N,N'-diphenylpiperazine is 164°.[4]

Acknowledgment.—We wish to thank Dr. Nelson R. Trenner of the Merck Laboratories, Rahway, N. J., for the infrared analysis.

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[1] S. Gabriel, *Ber.*, **21**, 1049 (1888); S. Gabriel and R. Stelzner, *ibid.*, **28**, 2929 (1895).

[2] W. J. Pearlman, THIS JOURNAL, **70**, 871 (1948).

[3] Analyses performed by Clark Microanalytical Laboratory, Urbana, Ill.

[4] D. S. Pratt and C. O. Young, THIS JOURNAL, **40**, 1428 (1918).

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Cyclic Vinyl Ethers as Reagents for the Introduction of Isoprene Units into Organic Compounds

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RECEIVED AUGUST 24, 1953

An extension of the previously described olefin synthesis[2,3] to 3-methyl-2,3-dihydrofuran (V) should offer a convenient method for the stepwise introduction of isoprene units into organic compounds which form Grignard reagents. Likewise, extension of the reaction to 4-methyl-3,4-dihydro-2H-pyran (I) should result in the formation of compounds structurally related to certain natural products (phytol, etc.). The availability[4] of the cyclic vinyl ethers I and V has permitted evaluation of these methods, and this report describes the synthesis of two new alkenols containing isoprene units.

The reaction of isobutylmagnesium bromide with the crude dichloride obtained from I and chlorine resulted in the formation of 2-isobutyl-3-chloro-4-methyltetrahydropyran (III) (35% yield), boiling at 60–75° (4 mm.). The boiling range and varia-

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[1] From the Ph.D. thesis of Howard Holmquist, University of Minnesota, 1951.

[2] *Cf.* (a) M. Jacobson, THIS JOURNAL, **72**, 1489 (1950); (b) R. Paul and O. Riobe, *Compt. rend.*, **224**, 474 (1947).

[3] (a) R. C. Brandon, J. M. Derfer and C. E. Boord, THIS JOURNAL, **72**, 2120 (1950); (b) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1707 (1950).

[4] W. E. Parham and H. E. Holmquist, THIS JOURNAL, **73**, 913 (1951).