Conversion of Enamines to Saturated Amines

Edwin L. Patmore and Harry Chafetz
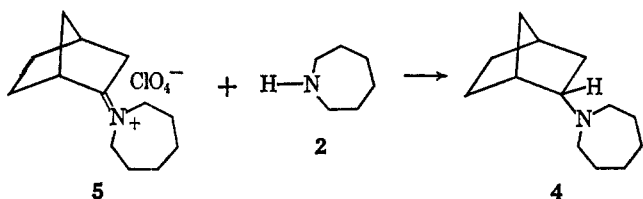
Contribution from Texaco, Inc., Beacon, New York

It was reported recently[1] that the *p*-toluenesulfonic acid catalyzed reaction of norcamphor (1) with hexamethylenimine (2) in refluxing xylene produces 2-N-hexamethyleniminobicyclo[2.2.1]hept-2-ene (3) and 2-N-hexamethyleniminobicyclo[2.2.1]heptane (4) in approximately equal amounts. The authors contend that
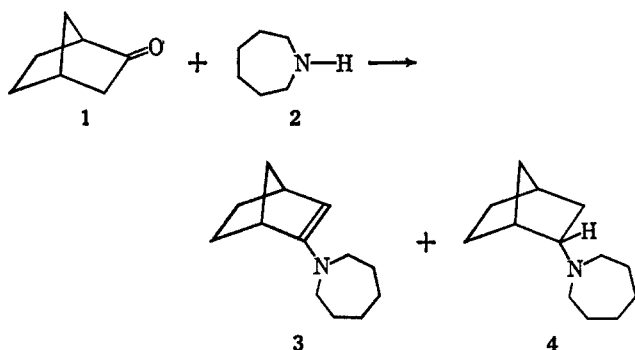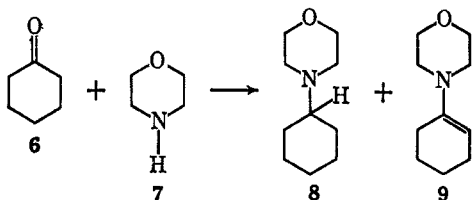

the saturated compound (4) is formed by reduction of the enamine (3) with hexamethylenimine, since they were able to convert N-2-bicyclo[2.2.1]heptylidenhexamethyleniminium perchlorate (5) to 2-N-hexamethyleniminobicyclo[2.2.1]heptane in 60% yield with an excess of hexamethylenimine. The oxidation products of the reaction were not determined. The reaction was assumed to be specific with respect to hexamethyl-

enimine, since other amines such as morpholine gave no isolable yield of saturated amine under their conditions.

In connection with other work we found that the *p*-toluenesulfonic acid catalyzed reaction of cyclohexanone (6) with morpholine (7) in refluxing toluene produces small quantities of N-cyclohexylmorpholine (8) in addition to the expected 1-morpholino-1-cyclo-

hexene (9). A distilled sample of 1-morpholino-1-cyclohexene was shown by vapor phase chromatography to contain both 8 and 9 in a weight ratio of 8/9 of 0.03.

(1) A. G. Cook, W. C. Meyer, K. E. Ungrodt, and R. H. Mueller, *J. Org. Chem.*, **31**, 14 (1966).

Additional experimental work proved that the concentration of N-cyclohexylmorpholine (8) could be increased by heating 1-morpholino-1-cyclohexene (9) with a catalytic amount of *p*-toluenesulfonic acid in a nitrogen atmosphere. Table I lists the reaction conditions and the results obtained. Six other unidentified products are formed in small amounts and a large amount of tar is formed (see the Experimental Section).

TABLE I
CONVERSION OF 1-MORPHOLINO-1-CYCLOHEXENE INTO N-CYCLOHEXYLMORPHOLINE AT 175–180°

Reacn time, hr	Wt % ratio of to
0	0.03
1	0.14
3	0.09
5	0.19
7	0.24
11	0.44
13	0.61
15	0.67
17	0.89
19	0.96
22	1.29

When 1-morpholino-1-cyclohexene was heated in a nitrogen atmosphere at 180° for 24 hr, no N-cyclohexylmorpholine was formed. A mixture of enamine and excess morpholine was heated at reflux (143–145°) for 52 hr. No N-cyclohexylmorpholine was formed.

In a similar manner, 1-pyrrolidino-1-cyclohexene was converted to N-cyclohexylpyrrolidine by heating with a catalytic quantity of *p*-toluenesulfonic acid in a nitrogen atmosphere. The results are listed in Table II.

TABLE II
CONVERSION OF 1-PYRROLIDINO-1-CYCLOHEXENE INTO N-CYCLOHEXYLPYRROLIDINE AT 180°

Reacn time, hr	Gas chromatographic area % ratio of to
0	0.02
1	0.10
4	0.13
8	0.14
12	0.18
16	0.20
22	0.22

No N-cyclohexylpyrrolidine was formed when 1-pyrrolidino-1-cyclohexene was heated in a nitrogen atmosphere in the absence of an acid catalyst.

Although detailed mechanistic studies were not conducted, the results suggest that the saturated amines are formed from the enamine by an initial protonation followed by an intermolecular hydride transfer from a second molecule of enamine. The driving force for this reaction would be the formation of an allylic cation which could subsequently react in several ways to give the observed products.[2]

(2) No N-phenylmorpholine was found among the products.

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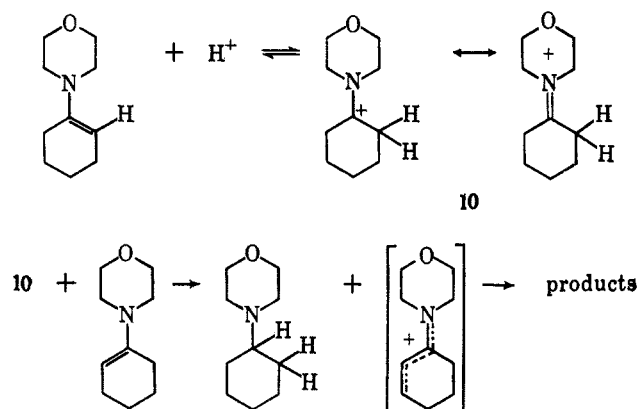
Enamines have been reduced previously to the corresponding saturated amines by heating with equimolar quantities of 98% formic acid.[3] The initial step was proved to be protonation followed by hydride transfer from the formate anion to form the saturated amine and carbon dioxide.

Experimental Section

Gas chromatographic analyses were performed on an Aerograph Model A-350-B chromatograph equipped with an Igepal Co-990 column (30 wt % on 60–80 mesh Chromosorb P packed in a 5 ft × 0.25 in. stainless steel column). Helium was used as the carrier gas (50 ml/min) and the column temperature was maintained at 204–205°. The relative areas of the enamine and saturated amine were measured by a Disc integrator and were converted to weight ratios by applying the appropriate weight relative response factors for the thermal conductivity detector. Infrared spectra were measured on a Perkin-Elmer Infracord Model 137B. The nmr spectra were measured in CDCl₃ solution using a Varian Associates V-4311 spectrometer operated at 60 Mcps. Tetramethylsilane was used as an internal reference standard. Mass spectra were measured on a Consolidated Electrodynamics Corp. Model 1030 spectrometer.

Materials.—1-Morpholino-1-cyclohexene, bp 109° (9 mm) [lit.[4] bp 104–106° (12 mm)] and 1-pyrrolidino-1-cyclohexene, bp 109–110° (16 mm) [lit.[4] bp 105–107° (13 mm)], were prepared by the method of Stork, Brizzolara, Landesmann, Szmuszkovicz, and Terrell[4] using catalytic quantities of p-toluenesulfonic acid. N-cyclohexylmorpholine (Abbott Laboratories) and p-toluenesulfonic acid monohydrate (Eastman Organic Chemicals) were used without further purification. Prepurified nitrogen (Air Reduction Co., Inc.) was used for the inert atmosphere.

Conversion of 1-Morpholino-1-cyclohexene to N-Cyclohexylmorpholine.—1-Morpholino-1-cyclohexene (33.4 g, 0.2 mole) and p-toluenesulfonic acid (1.0 g) were heated together at 175–180° for 24 hr in a nitrogen atmosphere. Gas chromatographic samples were obtained by hypodermic syringe inserted through a rubber septum and were taken at time 0 and hourly thereafter. The new product formed during the reaction was collected by preparative-scale gas chromatography and was identified as N-cyclohexylmorpholine by infrared, nmr, and mass spectra, and by gas chromatographic comparison of retention time and peak enhancement with an authentic sample. Distillation of the reaction mixture showed that 85.6% of the 1-morpholino-1-cyclohexene had been converted to products with a selectivity of 22.6% to N-cyclohexylmorpholine. Cyclohexanone (0.63 g), morpholine (1.47 g), higher boilers (0.4 g), and 12 g of residue were also obtained.

No N-cyclohexylmorpholine was formed when 1-morpholino-1-cyclohexene was heated in a nitrogen atmosphere at 175–180° for 23 hr. Excess morpholine was added to this mixture and it was heated for an additional 52 hr at reflux (143–145°). No N-cyclohexylmorpholine was formed.

Conversion of 1-Pyrrolidino-1-cyclohexene to N-Cyclohexylpyrrolidine.—1-Pyrrolidino-1-cyclohexene (30.2 g, 0.2 mole) and p-toluenesulfonic acid (1.0 g) were heated together at 178–180°

for 22 hr in a nitrogen atmosphere. Gas chromatographic samples were obtained by a hypodermic syringe inserted through a rubber septum and were taken at time 0 and hourly periods thereafter.

Samples of the new product formed during this reaction were collected by preparative-scale gas chromatography and identified by infrared, nmr, and mass spectra. The infrared spectrum showed absorptions at λ_{max}^{neat} 3.64 (s), 3.72 (s), 6.94 (s), 7.3 (m), 7.45 (m), 8.4 (m), 8.88 (s), 9.3 (w), 9.66 (w), 9.82 (w), 9.92 (w), and 11.3 (s) μ. The nmr spectrum (CDCl₃) showed unresolved multiplets centered at 1.23 and 1.78 ppm (15 protons) for the cyclic protons and an unresolved multiplet centered at 2.60 ppm (four protons) for the protons α to the nitrogen in the pyrrolidine ring. Mass spectral analysis showed the molecular weight to be 153. Other major peaks were observed at m/e 110, 97, 96, 70, 69, 55, 42, 41, and 39 which are characteristic of pyrrolidine and cyclohexylamine type structures.

Registry No.—9, 670-80-4; 8, 6425-41-8; 1-pyrrolidino-1-cyclohexene, 1125-99-1; N-cyclohexylpyrrolidine, 7731-02-4.

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Arylethanolamines from Diaroylfurazan Oxides

CARL R. MELOY AND DAVID A. SHIRLEY

*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916*

In a previous paper from this laboratory[1] the production of diaroylfurazan oxides from methyl aryl ketones was described. As a continuation of that work other furazans have been prepared by this method and these have been reduced by the use of lithium aluminum hydride to yield aryl-substituted ethanolamines.

Furazan oxides, containing two ArCO groups, are readily prepared by the action of nitric acid, containing a catalytic amount of nitrite ion, on aryl methyl ketones in acetic acid.
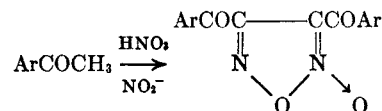
The reduction of furazan oxides (also commonly called furoxans) has been brought about with several different reducing agents including phosphorus pentachloride,[2] which removes the exocyclic oxygen atom to form a furazan, zinc and acetic acid,[3] which leads to dioximes, and sodium borohydride which also produces dioximes. In all these cases the 3,4 carbon–carbon bond in the 1,2,5-oxadiazole ring remains intact. Dornow, Fust, and Jordan[4] employed lithium aluminum hydride in the reduction of mixed furazan oxides to produce primary amines. They propose an initial cleavage of the furazan oxide to yield a nitrile and an anion of a nitro compound.

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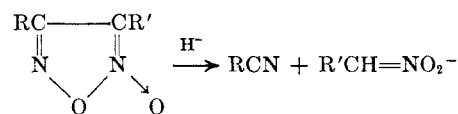
(1) D. A. Shirley, B. H. Gross, and M. J. Danzig, *J. Org. Chem.*, **23**, 1024 (1958).

(2) H. Wieland and L. Semper, *Ann.*, **358**, 36 (1907).

(3) R. Scholl, *Ber.*, **21**, 506 (1888); **23**, 3490 (1890).

(4) A. Dornow, K. J. Fust, and H. O. Jordan, *ibid.*, **90**, 2124 (1957).

(3) N. J. Leonard and R. R. Sauers, *J. Am. Chem. Soc.*, **79**, 6210 (1957).

(4) G. Stork, A. Brizzolara, H. Landesmann, J. Smuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).