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# Synthesis of Acetylhydrazines through Chloramination Reactions of Amides and Urethanes†

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The reactions of chloramine with the sodium salts of some amides and *N*-alkylurethanes have been carried out. The products were analyzed by infrared spectroscopy, mass spectroscopy, and nuclear magnetic resonance spectroscopy. It was shown that (1) chloramine reacts with the sodium salts of phenyl and aromatic amides such as acetanilide and *N*-benzoylbenzamide to give acetylphenylhydrazine and acetylarylhydrazines, respectively, (2) chloramine reacts with the sodium salts of aliphatic carboxamides such as *N*-methylacetamide to give the corresponding acetylhydrazine, and (3) chloramine reacts with the sodium salts of *N*-alkylurethanes such as *N*-ethylurethane to give 1-(ethoxycarbonyl)-1-alkylhydrazine, which can react with acetone to give the respective hydrazone of acetone.

## Introduction

During the past 4 decades, numerous researchers, largely from this laboratory and formerly from The Ohio State University, have examined the use of chloramine as an aminating agent for nucleophilic substances, notably nitrogen or phosphorus donor molecules. These studies have been particularly fruitful in the synthesis of various hydrazines and aminophosphine derivatives as well as a new class of compounds containing triazanium ions.[1-10]

The purpose of this study was to determine whether or not the chloramination reaction could be fruitfully applied to the synthesis of acylhydrazines, specifically to study the chloramination of the sodium salts of some amides and urethanes. Such a route to the formation of acylhydrazines would have the following advantages over previously developed pathways to these substances:[11-22] the procedure is relatively simple and should lead to high yields; the starting materials are readily available and of low cost; and the formation of the hydrazine derivatives would not require other hydrazines as starting materials.

Toward this objective, the chloraminations of the sodium salts of acetanilide, *N*-benzoylbenzamide, *N*-methylacetamide, and *N*-ethylurethane were studied and the corresponding hydrazine derivatives obtained, either pure or in identifiable mixtures.

## Experiments and Results

**Materials.** Acetanilide was supplied by Fisher Scientific Co.; *N*-benzylbenzamide, *N*-methylacetamide, *N*-ethylurethane, and sodium hydride were supplied by Aldrich Chemical Co. All were used as obtained after checking their purity by NMR spectrascopy.

Chloramine was prepared by using the Sisler-Mattair apparatus.[23] An ethereal solution of chloramine (0.1-0.4 M) was used in these reactions.

Analytical reagent grade solvents were either distilled or dried over sodium metal or size 3A molecular sieves prior to using and were then stored in airtight containers with polyethylene closure liners. All transfers were performed under nitrogen.

**Equipment.** All storing, transferring, or purification was done in a dry nitrogen atmosphere by using a KSE Model 2C 405R controlled-atmosphere box.

Distillations were carried out in a microlab standard taper 14/20 apparatus, which was equipped with an extra Vigreux column. The apparatus was insulated with glass wool to minimize heat loss.

Melting points were obtained in sealed capillary tubes in a Thomas-Hoover capillary melting-point apparatus and were reported uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Infrared spectra were recorded on a Perkin-Elmer 283 B infrared spectrophotometer. Samples of the products were examined in KBr pellets or as Nujol mulls on sodium chloride plates. Table I shows the infrared spectral data for some of the prepared hydrazine derivatives.

**Table I.** Infrared Absorption Bands[a] in $cm^{-1}$

| | |
|---|---|
| $CH_3CO-N(C_6H_5)-NH_2$ | 3325 (s), 3220 (s), 3060 (s), 1645 (sh), 1630 (br), 1595 (m), 1585 (m), 1495 (m), 1460 (w), 1395 (br), 1345 (w), 1325 (w), 1290 (m), 1253 (s), 1180 (s), 1160 (s), 1075 (m), 1045 (w), 1020 (w), 960 (s), 930 (w), 905 (w), 765 (s), 720 (w), 700 (s), 610 (m), 598 (m), 570 (m), 515 (m), 460 (br), 380 (br), 275 (br) |
| $C_6H_5CO-N(CH_2C_6H_5)-NH_2$ | 3330 (m), 2950 (br), 1920 (w), 1895 (m), 1600 (br), 1490 (w), 1445 (br), 1378 (m), 1355 (w), 1320 (w), 1260 (br), 1205 (w), 1178 (m), 1155 (w), 1070 (br), 1022 (m), 998 (w), 972 (s), 930 (br), 870 (br), 785 (s), 755 (s), 715 (br), 700 (sh), 690 (sh), 630 (sh), 615 (s), 550 (s), 515 (w), 482 (s), 455 (sh), 440 (s), 390 (s), 370 (br), 280 (s), 240 (m) |

[a] Key: br, broad; d, doublet; m, medium; s, strong; sh, shoulder; w, weak.

Proton nuclear magnetic resonance spectra were recorded on a Varian EM 360L NMR spectrometer or Nicolet NT 300 spectrometer operating at a field strength of 7 T. Carbon-13 as well as nitrogen-15 measurements were recorded on a FT 300-MHz multinuclear spectrometer. Chloroform-*d* ($CDCl_3$) or dimethyl-$d_6$ sulfoxide ($(CD_3)_2SO$) was used as solvent and TMS ($Si(CH_3)_4$) as the internal standard reference. All chemical shifts are reported with the convention that a positive $\delta$ value corresponds to a chemical shift to a higher frequency. The NMR spectral data are shown in Tables II and III.

Electron-impact mass spectra were obtained on an AEI MS-30

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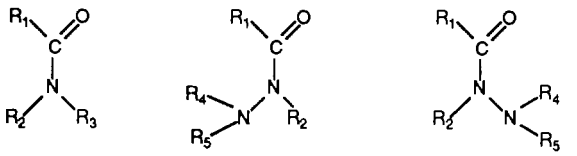
0020-1669/90/1329-0309$02.50/0 

**Table II.** 300-MHz $^1$H NMR Data[a]



*E* form *Z* form

| compd | solvent | $\delta(R_1)$, ppm | $J$, Hz | $\delta(R_2)$, ppm | $J$, Hz | $\delta(R_3)$, ppm | $J$, Hz | $\delta(R_4 + R_5)$ |
|---|---|---|---|---|---|---|---|---|
| acetanilide | | | | | | | | |
| $CH_3CO-NH-C_6H_5$ | $CDCl_3$ | 2.117 (s) | | 7.069 (5) (*p*) | $^1J$ = 6.34<br>$^2J$ = 1.04 | 8.446 (s, b) | | |
| | | | | 7.254 (5) (*m*) | $^1J$ = 5.30<br>$^2J$ = 1.40 | | | |
| | | | | 7.498 (d) (*o*) | $^1J$ = 5.70<br>$^2J$ = 1.53 | | | |
| 1-acetyl-1-phenylhydrazine | | | | | | | | |
| $CH_3CO-N(C_6H_5)-NH_2$ | $CDCl_3$ | 1.999 (s) | | 7.2–7.6 (m) | $^1J$ = 7.84<br>$^2J$ = 14.79 | | | 4.1–4.6 (b) |
| *N*-benzoylbenzamide | | | | | | | | |
| $C_6H_5CO-NH-C_6H_5CH_2$ | $CDCl_3$ | 7.17–7.78 (m) | $^1J$ = 10.27<br>$^2J$ = 7.64 | 4.422 (d)<br>7.17–7.78 (m) | $J$ = 5.89<br>$^1J$ = 10.27<br>$^2J$ = 7.64 | 7.343 (t) | $^1J$ = 7.29 | |
| 1-benzoyl-1-benzylhydrazine | | | | | | | | |
| $C_6H_5CO-N(C_6H_5CH_2)-NH_2$ | $CDCl_3$ | 7.20–7.60 (m) | $J$ = 7.08 | 4.68 (s)<br>7.20–7.60 (m) | <br>$J$ = 7.08 | | | 4.32 (b, s) |
| *N*-methylacetamide | | | | | | | | |
| $CH_3CO-NH-CH_3$ | $CDCl_3$ | 1.977 (s) | | 2.758 (d) | $J$ = 5.75 | 7.396 (b, m) | $J$ = 1.15 | |
| 1-acetyl-1-methylhydrazine | | | | | | | | |
| $CH_3CO-N(CH_3)-NH_2$ | $CDCl_3$ | 2.111 (*Z*)<br>2.199 (*E*) | | 3.179 (*Z*)<br>3.243 (*E*) | | | | 4.250 (*Z*) |
| *N*-ethylurethane | | | | | | | | |
| $CH_3CH_2OCO-NH-CH_3CH_2$ | $CDCl_3$ | 1.156 (t)<br>4.107 (q) | $J$ = 7.1<br>$J$ = 6.5 | 1.227 (t)<br>3.199 (q) | $J$ = 7.1<br>$J$ = 6.5 | 5.623 (s, b) | | |
| 1-(ethoxycarbonyl)-1-ethylhydrazine | | | | | | | | |
| $CH_3CH_2OCO-N(CH_3CH_2)-NH_2$ | $CDCl_3$ | 1.131 (t)<br>3.219 (q) | $J$ = 7.1<br>$J$ = 6.5 | 1.227 (t)<br>4.104 (q) | $J$ = 7.1<br>$J$ = 6.5 | | | |
| 1-(ethoxycarbonyl)-1-ethylhydrazone of acetone | | | | | | | | |
| $CH_3CH_2OCO-N(CH_3CH_2)-N=C(CH_3)-CH_3$ | DMSO-$d_6$ | 1.13 (5)<br>3.20 (q) | $J$ = 7.0<br>$J$ = 6.5 | 1.20 (t)<br>4.10 (q) | $J$ = 7.0<br>$J$ = 6.5 | | | 1.799 (s)<br>2.007 (s) |

[a] Key: s, singlet; d, doublet; t, triplet; b, broad; m, multiplet; q, quartet; 5, pentet; *E*, entgegen (opposite); *Z*, zusammen (together).

mass spectrometer operating at 70 eV and equipped with a DS-30 data system. The major fractions of some of the products are included in Table IV.

The constituents of the liquid reaction products were determined using a Varian Model 3700 gas chromatograph equipped with a flame-ionization detector, a 6-ft Carbowax column containing 10% Carbowax 20M + 5% KOH, along with a CDS-111 data analyzer and a Soltic Model 252 integrator recorder. Unless otherwise stated, the chromatograms were obtained by using the following parameters: injector temperature, 200 °C; column temperature, 140 °C; helium flow rate, 30 mL/min; flame-ionization detector temperature, 200 °C.

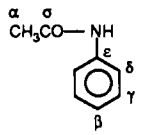
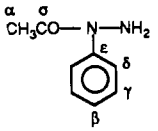
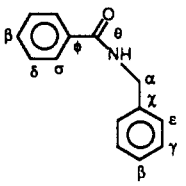
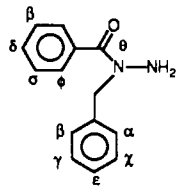
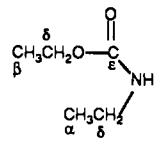
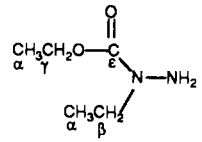
**Preparation of the Sodium Salts of Carboxamides and Urethanes.** Into a dry three-neck, round-bottom flask, equipped with stirrer, reflux condenser, and addition funnel, 1.4 g of sodium hydride and 50 mL of xylene, which had been dried over sodium metal, were introduced. There was then added 0.05 mol of the amide or urethane in 200 mL of boiling xylene and the mixture refluxed with stirring for 12–24 h, under an atmosphere of nitrogen, during which time the white sodium salt precipitated. The condenser was then removed and xylene allowed to evaporate under a stream of nitrogen.

**Preparation of 1-Acetyl-1-phenylhydrazine.** To 0.05 mol of the sodium salt of acetanilide was added 300 mL of 0.21 M $NH_2Cl$ solution in diethyl ether gradually through the addition funnel and the reaction mixture refluxed for 6 h with continuous stirring. The mixture was filtered. The residue, which had reducing activity toward acidified $KIO_3$ solution, was then extracted with warm chloroform, and the chloroform solution was chilled. Yellowish flaky crystals precipitated. Another portion of the product was obtained by adding diethyl ether to the solution, which was then cooled. A total of 6.3 g of $CH_3CON(C_6H_5)NH_2$ was obtained (85% yield). The melting point was 119–120 °C. Anal. Calcd for $CH_3CON(C_6H_5)NH_2$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.76; H, 6.54; N, 18.52. A satisfactory proton NMR and carbon-13 spectral analysis[24] was obtained (Tables II and III).

The nitrogen-15 spectrum shows a triplet centered at about −299.944 ppm ($J$ = 39.29 Hz), which is assigned to $NH_2$; the expected singlet for $R_2N$ did not show in the spectrum, probably because it falls outside the scanned range.

(24) Khatib, A. A. *Studies of Chloramine Reactions in the Synthesis of Substituted Hydrazines and Triazanium Salts*; University Microfilm International: Ann Arbor, MI, 1985; Order No. DA89523847.

**Table III.** FT 300-MHz $^{13}C$ NMR Data[a]

| compound | δ, ppm | assignt | *J*, Hz |
|---|---|---|---|
|  | 23.608 | α | |
| | 119.782 | β | |
| | 123.633 | γ | |
| | 128.186 | δ | |
| | 137.569 | ε | |
| | 168.890 | σ | |
|  | 21.214 (q) | α | $^1J$ = 6.25, $^2J$ = 1.87 |
| | 127.250 (t) | β | $^1J$ = 7.91, $^2J$ = 11.11 |
| | 128.837 (t) | γ | $^1J$ = 10.13, $^2J$ = 16.41 |
| | 136.485 (t) | δ | $^1J$ = 3.65, $^2J$ = 30.53 |
| | 142.293 (s) | ε | |
| | 168.750 (s) | σ | |
|  | 43.411 | α | |
| | 126.830 | β | |
| | 126.898 | γ | |
| | 127.222 | δ | |
| | 128.017 | ε | |
| | 128.162 | σ | |
| | 130.998 | χ | |
| | 133.991 | φ | |
| | 138.260 | θ | |
|  | 30.818 | α | |
| | 126.849 | β | |
| | 127.177 | γ | |
| | 127.759 | δ | |
| | 128.219 | ε | |
| | 128.778 | σ | |
| | 129.978 | χ | |
| | 130.131 | φ | |
| | 135.928 | θ | |
|  | 14.087 | α | |
| | 14.624 | β | |
| | 35.171 | γ | |
| | 59.848 | δ | |
| | 156.386 | ε | |
|  | 12.154 | α | |
| | 44.746 | β | |
| | 61.249 | γ | |
| | 127.809 | ε | |

[a] See Table II for key.

The IR spectrum shows the characteristic peaks for $NH_2$ at 3325, 3220, 3060, and 1595 $cm^{-1}$. The peak for carbonyl is a broad peak at 1630 $cm^{-1}$.

The mass spectrum shows the peak at $m/e$ = 150 for the molecule; the fractions originate from a component structurally analogous to phenylhydrazine, $(C_6H_8N_2)^{\cdot+}$, at $m/e$ = 108.

**Preparation of 1-Benzoyl-1-benzylhydrazine.** To 0.05 mol of the sodium salt of *N*-benzoylbenzamide was added 300 mL of 0.20 M $NH_2Cl$ solution in ethyl ether gradually through an addition funnel and the reaction mixture refluxed for 8 h with continuous stirring. The liquid was allowed to evaporate under a stream of nitrogen, leaving a gummy residue that reduced acidified $KIO_3$ solution. The solid product was extracted with a mixture of acetone, ethanol, and diethyl ether with a volume ratio 3:1:1 respectively. When the extract was cooled, small, white crystals formed. A total of 6.2 g of $C_6H_5CO(C_6H_5CH_2)NNH_2$ was collected (55% yield). The melting point was 64–65 °C. Anal. Calcd: C, 74.32; H, 6.21; N, 12.38. Found: C, 74.24; H, 6.25; N, 12.17. A satisfactory proton NMR and carbon-13 spectral analysis (Tables II and III) was obtained.

The IR spectrum shows the characteristic peaks for $NH_2$ at 3330 and 1600 $cm^{-1}$ and the carbonyl peak at 1600 $cm^{-1}$.

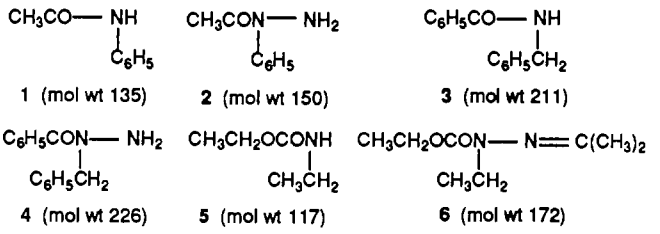
The mass spectrum shows the molecular ion peak $m/e$ = 226.

**Reaction of Chloramine with the Sodium Salt of *N*-Methylacetamide.** To 0.05 mol of the sodium salt of *N*-methylacetamide was added 300 mL of 0.20 M $NH_2Cl$ solution in ethyl ether gradually, and the reaction mixture was refluxed for 8 h with continuous stirring. The solid formed proved to be sodium chloride, which was filtered out and discarded. The diethyl ether was stripped off. A sample of the remaining yellowish liquid, which reduced acidified $KIO_3$ solution, was injected into the gas chromatograph; two peaks with retention times of 1.74 and 2.23 min resulted. The first corresponds to *N*-methylacetamide (indicated by increase in the area of the peak at 1.74 min upon the addition of pure *N*-methylacetamide) and the other was assigned to 1-acetyl-1-methylhydrazine. The ratio of the two peaks was 53.0:47.0.

The elemental analyses agreed with the above assignment. Anal. Calcd for (53% $CH_3CON(CH_3)NH_2$ + 47% $CH_3CONH(CH_3)$): C, 44.86; H, 9.33; N, 25.87. Found: C, 43.86; H, 9.92; N, 24.95.

The proton NMR spectrum shows peaks at 1.977, 2.758, and 7.396 ppm, which are assigned to $CH_3CO$–, $CH_3N$–, and N–H protons of N–methylacetamide, respectively. The peaks at 2.111, 3.179, and 4.250 ppm are assigned to $CH_3CO$–, $CH_3N$–, and $NH_2$ protons of (*Z*)-1-acetyl-1-methylhydrazine respectively. The peaks at 2.199, 3.243, and 4.609 ppm are assigned to $CH_3O$–, $CH_3N$–, and $NH_2$ protons of (*E*)-1-acetyl-1-methylhydrazine, respectively (Table II).

**Table IV.** Mass Spectral Data




| MS, *m/e* | rel abundance | | | | | |
|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** |
| 226 | | | | 4 | | |
| 212 | | | 12 | | | |
| 211 | | | 65 | 15 | | |
| 210 | | | 26 | | | |
| 181 | | | 2 | | | |
| 172 | | | | | | 16 |
| 157 | | | | | | 8 |
| 150 | | 13 | | | | |
| 135 | 3 | 8 | | | | |
| 129 | | | | | | 6 |
| 117 | | | | | 9 | |
| 116 | | | | | | 7 |
| 108 | | 100 | | | | |
| 106 | | | 22 | 18 | | |
| 105 | | | 100 | 100 | | |
| 102 | | | | | 23 | 18 |
| 93 | 100 | 33 | | | | |
| 92 | | 21 | | | | |
| 91 | | 16 | 11 | 24 | | |
| 89 | | | | | 8 | |
| 88 | | | | | 22 | 16 |
| 81 | | 2 | | | | |
| 79 | | 10 | 6 | 3 | | |
| 78 | | 8 | 7 | 8 | | |
| 77 | 5 | 26 | 61 | 61 | | |
| 72 | | | | | 22 | 21 |
| 71 | | | | | 4 | 16 |
| 66 | 18 | 4 | | | | |
| 65 | 10 | 8 | 7 | 9 | | |
| 64 | 2 | 5 | 1 | 1 | | |
| 63 | 3 | 3 | 3 | 3 | | |
| 56 | | | | | 11 | 44 |
| 51 | 4 | 11 | 22 | 23 | | |
| 45 | | | | | 12 | 10 |
| 44 | | | | | 44 | 51 |
| 43 | 25 | 36 | | | 8 | 23 |
| 42 | | | | | 7 | 22 |
| 39 | 10 | 8 | 6 | 9 | | |
| 30 | | | | | 100 | 58 |
| 29 | | 8 | | 4 | 84 | 80 |
| 28 | 9 | 20 | 10 | 38 | 22 | 100 |

**Reactions of Chloramine with the Sodium Salt of *N*-Ethylurethane.** To 30 mL of liquid ammonia was added 0.05 mol of the sodium salt of *N*-ethylurethane. Approximately 0.1 mol of chloramine from the generator was passed into the solution at −78 °C. The ammonia was allowed to evaporate. The remaining mixture was extracted with 30 mL of acetone. After the solvent was stripped off, 1.2 g of a colorless liquid remained. The mass spectrum of this liquid shows the molecular ion at *m/e* 172, which is the molecular mass of $CH_3CH_2OCON(CH_3CH_2)N{=}C(CH_3)_2$. Anal. Calcd for 77% $CH_3CH_2OCON(CH_3CH_2)N{=}C(CH_3)_2$ + 23% $CH_3CH_2OCONH(CH_3CH_2)$: C, 54.76; H, 9.32; N, 15.29. Found: C, 53.20; H, 9.31; N, 15.27.

The proton NMR spectrum shows peaks at 1.13 and 3.20 ppm, 1.20 and 4.20 ppm, and 1.799 and 2.007 ppm, which are assigned to $CH_3CH_2O$–, $CH_3CH_2N$–, and $=C(CH_3)_2$ protons, respectively (Table II).

The nitrogen-15 spectrum shows two kinds of singlets centered at −63.276 and −294.389 ppm, which are assigned to N=C and ROOC—N, respectively.

To 100 mL of diethyl ether was added 0.05 mol of the sodium salt of *N*-ethylurethane. Approximately 0.1 mol of chloramine from the generator was passed into the solution. The resulting solid was filtered off and the diethyl ether allowed to evaporate under a stream of nitrogen. A sample of the remaining colorless liquid, which reduced acidified $KIO_3$ solution, was injected into the gas chromatograph. Two peaks with retention times of 0.47 and 0.57 min. resulted. The first corresponds to *N*-ethylurethane (indicated by increase in the area of the peak at 0.47 min. upon the addition of pure *N*-ethylurethane) and the other was assigned to $CH_3CH_2OCON(CH_3CH_2)NH_2$. The ratio of the two peaks was 57:43.

Anal. Calcd for 57% $CH_3CH_2OCONH(CH_3CH_2)$ + 43% $CH_3CH_2OCON(CH_3CH_2)NNH_2$: C, 48.26; H, 9.18; N, 15.81. Found: C, 49.45; H, 9.46; N, 15.19.

The proton NMR spectrum shows peaks at 1.131 and 3.219 ppm, 1.227 and 4.104 ppm, and 4.196 ppm, which are assigned to $CH_3CH_2O$–, $CH_3CH_2N$–, and $NH_2$ protons, respectively (Table II).

The carbon-13 NMR spectrum shows eight different carbons; the peaks at 14.209, 35.207, 59.877, and 156.313 ppm are assigned to $CH_3$, $CH_2N$, $CH_2O$, and C=O carbons of *N*-ethylurethane, respectively. The other peaks at 12.154, 44.746, 61.249, and 127.809 ppm are assigned to $CH_3$, $CH_2N$, $CH_2O$, and C=O of $CH_3CH_2OCON(CH_3CH_2)NH_2$, respectively (Table III).

## Discussion

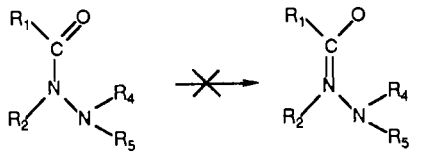
The reactions of chloramine with several of the sodium salts of amides and urethanes have been examined. The following conclusions have been reached: (1) the reaction of chloramine with the sodium salt of acetanilide yields 1-acetyl-1-phenylhydrazine. (2) The reaction of chloramine with the sodium salt of *N*-benzoylbenzamide yields 1-benzoyl-1-benzylhydrazine. (3) The reaction of chloramine with the sodium salt of *N*-methylacetamide yields 1-acetyl-1-methylhydrazine. (4) The reaction of chloramine with the sodium salt of *N*-ethylurethane yields 1-(ethoxycarbonyl)-1-ethylhydrazine. Acetone reacts with the latter, yielding the 1-(ethoxycarbonyl)-1-ethylhydrazone of acetone.

The general method of preparation introduced here[25] is a simple, practical way to produce hydrazines and hydrazine derivatives. The compounds $C_6H_5C(O)—N(CH_2C_6H_5)NH_2$, $CH_3CH_2OOC—N(CH_2CH_3)NH_2$ and $CH_3CH_2OOC—N(CH_2CH_3)N{=}C(CH_3)_2$ are new. This class of compounds, acylhydrazines, may be of importance as rocket fuels, as 1,1-dimethylhydrazine precursors, and as pharmaceuticals, photographic chemicals, or polyolefin stabilizers.

The proton NMR spectra of the prepared acylhydrazines and (ethoxycarbonyl)hydrazines have been examined, and the following conclusions have been reached: (1) The shielding, and thus the chemical shift, of the amide proton is affected by the polar and resonance character of the substituents. (2) The substituents on one nitrogen exert very little effect on the hydrogens on the other nitrogen of a hydrazine derivative. (3) *N*-Ethylurethane as well as its hydrazine derivative are present as single isomers. (4) Only 1-acetyl-1-methylhydrazine, of those studied, shows the two isomeric rotamers.

The amide proton chemical shifts for acetanilide, *N*-methylacetamide, and *N*-benzylbenzamide (Table II) are 8.446 ($J$ = 1 Hz), 7.396 ($J$ = 1 Hz), and 7.343 ppm ($J$ = 7 Hz), respectively. The phenyl group resonance which renders the nitrogen in acetanilide more positive causes the downshift of the amide proton to be significantly more than the rest. However, the amide proton of *N*-ethylurethane (Table II) is at higher field than those of the other studied amides; this may have resulted from the carboxyl resonance between the carbon and the two oxygens rather than the oxygen and nitrogen of carboxamides.

It is clearly shown, as expected, that $R_4$ and $R_5$ chemical shifts (Table II) are not influenced significantly by the substituents on the other nitrogen, which would not support the suggested formation of intrahydrogen bonding[26-28] between $R_4$ and $R_5$ and the carbonyl group. Moreover, ethylurethane and its hydrazine derivative are present as single isomers, which does not support the possibility of double-bond formation between the carbonyl carbon and nitrogen.



Of all the acetylhydrazines studied only 1-acetyl-1-methylhydrazine showed the rotameric isomers (*E* and *Z*). A possible explanation for the others not showing the rotameric isomer is the presence of a phenyl group, which through its resonance makes the formation of such rotamers unlikely.

Finally, it is worth mentioning here that the coupling constant $J_{NH}$–$J_{R_2}$ is always about 6 Hz; in *N*-methylacetamide, the methyl protons ($R_2$) form a doublet ($J$ = 5.75 Hz); in *N*-benzoylbenzamide the methylene protons ($R_2$) form a doublet ($J$ = 5.98 Hz). These protons are singlets in their respective hydrazine derivatives.

The mass spectra of the prepared acetylhydrazines along with their parent amines have been examined, and it has been observed that the elimination of small neutral fragments from acetanilide (**1**), 1-acetyl-1-phenylhydrazine (**2**), *N*-benzoylbenzamide (**3**), and 1-benzoyl-1-benzylhydrazine (**4**) to give the radical cations of phenylamine ($[C_6H_7N]^{\bullet+}$), phenylhydrazine ($[C_6H_8N_2]^{\bullet+}$), and phenylaldehyde ($[C_7H_6O]^{\bullet+}$), respectively, fits expected fragmentation patterns.

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**Registry No.** $CH_3CONHPh$, 103-84-4; $PhCONHCH_2Ph$, 614-28-8; $CH_3CONHCH_3$, 79-16-3; EtOCONHEt, 2597-54-8; $NH_2Cl$, 10599-90-3; $CH_3CON(Ph)NH_2$, 2116-41-8; $PhCON(CH_2Ph)NH_2$, 38663-32-0; $CH_3CON(CH_3)NH_2$, 3530-13-0; $EtOCON(Et)N{=}C(CH_3)_2$, 124153-85-1; $EtOCON(Et)NH_2$, 124153-86-2.

(25) Recently, a similar idea was patented: Brit. Pat. 1,561,146 (Cl. CO/B21/16), Feb 12, 1980; Appl. 76/42,306, Oct 1976. Earlier Jander (Jander, J. *Z. Anorg. Allg. Chem.* **1955**, *280*, 264, 276; *Naturwissenschaften* **1955**, *42*, 178) mentioned the reaction between potassium amide and chloramine to produce hydrazine.

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