60%; $[\alpha]_{578}$ -15° (c 0.68, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 3.6 (m, 1 H), 3.2 (d, 1 H), 2.3–1.3 (m, 4 H), 1.1 (s, 3 H), 1.0 (s, 3 H). Anal. Calcd: C, 68.54; H, 8.63. Found: C, 67.79; H, 8.65.

(*R*)-(+)-2-Cyclohexenol (3). $LiAlH_4$ (1.69 g, 44 mmol) was suspended in ca. 300 mL of dry ether. Quinine (44 mmol, 14.24 g) was added, and the suspension was refluxed for 15 min. After the mixture was cooled to 0 °C, 3.84 g of cyclohexenone (40 mmol) dissolved in 10 mL of ether was added, and stirring was maintained for 1 h at 0 °C. Water was added (ca. 5 mL) followed by 10% H_2SO_4 until all of the solid had disappeared. The water layer was extracted with ether (3 × 50 mL). The organic layer was dried ($MgSO_4$) and evaporated, yielding 2.6 g of cyclohexenol (58%), $[\alpha]_{578}$ +21.7° (c 1.95, CH_2Cl_2).

***cis*-2,3-Epoxycyclohexanol [(+)-4].** Cyclohexenol (1.5 g) ($[\alpha]_{578}$ +21.8) and 3.1 g of *m*-chloroperbenzoic acid (85% purity) were dissolved in CH_2Cl_2 at 0 °C. After the mixture was sitrred for 16 h, it was filtered and the organic layer extracted with dilute NaOH solution and H_2O. The organic layer was dried ($MgSO_4$) and evaporated, yielding 0.85 g of epoxide: $[\alpha]_{578}$ +6.4° (c 2.05, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 4.0 (m, 1 H), 3.3 (s, 2 H), 2.8 (s, OH), 2.0–1.0 (m, 6 H).

(*S*,*S*)-(-)-2,3-Epoxycyclohexanone. *cis*-2,3-Epoxycyclohexanol (0.85 g) ($[\alpha]_{578}$ +6.4), 1.44 g of sodium acetate, and 3.55 g of pyridinium chlorochromate were suspended in CH_2Cl_2, and the solution was stirred for 6 h. Ether was added, and the mixture was filtered over florisil. The organic layer was extracted with $NaHCO_3$ solution and with H_2O. After the solution was dried and evaporated, the product was obtained: yield 0.3 g; $[\alpha]_{578}$ -19° (c 1.54, CH_2Cl_2).

(*S*)-(-)-2-Cyclohexenol. To a solution of 2.2 g of (*S*,*S*)-(-)-2,3-epoxycyclohexanone in 25 mL of MeOH at 0 °C were added a few drops of acetic acid and 2.5 mL of hydrazine hydrate, and after the solution had been stirred for 0.5 h, it was evaporated. Water was added and extracted with ether. After drying ($MgSO_4$) and evaporating the organic layer, crude product was obtained. Distillation gave 0.93 g of pure (*S*)-(-)-2-cyclohexenol: yield 48%; $[\alpha]_{578}$ -15° (c 1.28, CH_2Cl_2).

Determination of the Enantiomeric Excess of Alcohol 3. Following the procedure described by Mosher,[21] the ester of the alcohol 3 ($[\alpha]_{578}$ +21°) was prepared, and its ^1H and ^{19}F NMR were determined: ^1H NMR ($CDCl_3$) δ 7.6–7.4 (m), 6.0–5.5 (m), 3.6 (s), 2.1–1.6 (m); ^{19}F NMR ($CFCl_3$) δ 72.1 (two signals).

Registry No. 1a, 930-68-7; **1b**, 4694-17-1; **1c**, 6553-64-6; **2a**, 72029-30-2; **2b**, 72003-85-1; **2c**, 72003-86-2; (*R*)-**3**, 3413-44-3; (*S*)-**3**, 6426-26-2; **4**, 72029-31-3.

Notes

Application of *N*-Phenyltrifluoromethanesulfonamides to the Synthesis of Pyrazines

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Introduction

The pyrazines have long been of interest to medicinal chemists. These compounds, many of which are natural products, have proven to be useful as antibiotics,[2] tuberculostatics,[3] diuretics,[4] organoleptics,[5] and antitumor agents.[6]

The two most common routes to these heterocycles involve either the self-condensation of α-amino ketones[7] or the condensation of 1,2-dicarbonyl compounds with 1,2-diamines,[8] followed by oxidation of the resulting dihydropyrazines to the corresponding pyrazines.[9] As with most synthetic methods, the utility of the sequence is limited by the accessibility of the starting materials. Unfortunately, none of the above starting materials is easily synthesized in high yield, and at least one group of them, the α-amino ketones, has the added problem of instability.

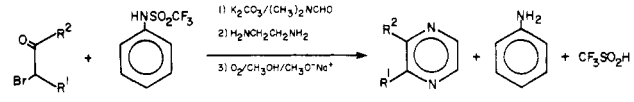
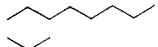


Figure 1. Reaction scheme for the synthesis of the pyrazines from the corresponding α-imino ketones.

Table I

R^1	R^2	yield, %
	CH_3	70
	CH_3	65
	CH_3	60
	CH_3	64

Results and Discussion

This investigation is directed at improving the diamine sequence described above. Our scheme emphasizes the synthesis of a reactive imino ketone intermediate which can be condensed with the appropriate diamine and the resulting dihydropyrazine oxidized to the corresponding pyrazine. The sequence proceeds in good yield and does not require the isolation of intermediates.

In an earlier investigation we determined that *N*-phenyltrifluoromethanesulfonamides could be alkylated

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in high yield with a variety of alkyl halides and α-halo ketones under mild conditions.[10] When the alkylating agents were α-halo ketones or aldehydes, we observed that even under the mildest reaction conditions, i.e., in K_2CO_3/acetone, the elements of CF_3SO_2H were eliminated from the product.

We have now shown that these α-imino ketones when reacted with diamines followed by oxidation with molecular oxygen under basic conditions produce pyrazines. Furthermore, the starting α-halo ketones or aldehydes for the sequence are accessible in high yield through a variety of different techniques. The scheme is summarized in Figure 1. The yields of a number of pyrazines prepared by this method are summarized in Table I.

In general, the procedure involves alkylation of *N*-phenyltriflamide with an α-bromo ketone in DMF at 80 °C with K_2CO_3 as the base. The elimination to the imino ketone can be effected concurrently with the alkylation by using an excess of K_2CO_3, or, alternatively, the alkylation product can be isolated. However, owing to their instability, neither the imino ketones nor the dihydropyrazines were isolated. The condensation of the imino ketone with the diamine was carried out on the crude imino ketone by using a slight excess of the diamine. Although the dihydropyrazines were not isolated, the reactions were followed by GC/MS which indicated the major products to be aniline and the dihydropyrazine. At this point, the reaction mixture was added to an oxidizing media consisting of O_2/NaOH/CH_3OH. The resulting pyrazines were easily isolated by standard procedures.

Experimental Section

Materials. Trifluoromethanesulfonic anhydride (triflic anhydride) and *N*-phenyltrifluoromethanesulfonamide (phenyltriflamide) were prepared as previously described by Hendrickson et al.[11]

The infrared (IR) spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. The ^1H NMR spectra were recorded on a Varian EM 360 spectrometer; the chemical shifts are given in parts per million relative to internal Me_4Si. Mass spectra were taken on a Du Pont 21-490 mass spectrometer. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. VPC analyses were done on a Hewlett-Packard 5710A equipped with a thermal conductivity detector and using a glass column packed with 5% SF96 on Chromosorb WAW, DMCS, or on a Varian Aerograph 1400 equipped with a flame ionization detector and using a glass column packed with 10% SE30 on Chromosorb WAW, DMCS. Preparative thin-layer plates (silica gel GF) were supplied by Analtech, Inc.

5-Methyl-3-bromo-2-hexanone. This compound was prepared from 5-methyl-2-hexanone in 96% yield by using the method described by Bauer and Macomber.[12] The product was distilled, bp 41–44 °C (30 mmHg), and an analytical sample collected by gas chromatography: IR (neat) 2956, 1714, 1460, 1351 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.32 (t, 1, J = 7.2 Hz), 2.38 (s, 3), 1.80 (m, 3, CH and CH_2), 0.98 (m, 6, CH_3's); mass spectrum, m/e (rel intensity) 195, 194, 193, 192 (>1), 138 (12), 136 (13), 43 (100); m/e 195 and 193 are due to ion–molecule interactions (p + 1). Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.79. Found: C, 43.85; H, 6.71.

3-Bromo-2-undecanone. Bromination of 2-undecanone was effected by using the method of Davies and Summers.[13] The yield of 3-bromo-2-undecanone was quantitative; bp 141–143 °C (17 mmHg). An analytical sample was collected by gas chromatography: IR (neat) 2930, 2957, 1724, 1458, 1354, 1222, 1147 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.23 (t, 1, J = 6.8 Hz), 2.33 (s, 3), 1.98 (m, 2), 1.29 (m, 12, CH_2's), 0.89 (t, 3, J = 5 Hz); mass spectrum, m/e (rel intensity) 251, 250, 249, 248 (<1), 138 (12), 136 (11), 71 (7), 55 (7), 43 (100); m/e 251 and 249 are due to ion–molecule interactions. Anal. Calcd for $C_{11}H_{21}BrO$: C, 53.03; H, 8.49. Found: C, 53.21; H, 8.24.

2-Isobutyl-3-methylpyrazine. *N*-Phenyltriflamide (4.82 g, 0.0214 mol) was alkylated with 3-bromo-5-methyl-2-hexanone (3.84 g, 0.02 mol) in DMF by using K_2CO_3 as base at 80 °C.

A sample of the *N*-[3-(5-methyl-2-oxohexyl)]-*N*-phenyltriflamide was purified by preparative thin-layer chromatography on a 20 cm × 20 cm × 2000 μm silica gel plate, eluting with 9:1 petroleum ether:ether (v/v). The product was recovered in 80% yield. IR (neat) 2951, 1730, 1223, 1191, 1148, cm^{-1}; ^1H NMR ($CHCl_3$) δ 7.41 (s, 5), 4.82 (dd, 1), 2.29 (s, 3), 2.00–1.20 (m, 3, CH_2 and CH), 0.95 (dd, 6, J = 6 and 6 Hz); mass spectrum, m/e (rel intensity) 337 (0), 294 (2), 161 (38), 146 (22), 119 (100), 104 (6), 77 (31), 43 (27). Anal. Calcd for $C_{14}H_{18}F_3NO_3S$: C, 49.84; H, 5.38. Found: C, 50.06; H, 5.64. The alkylation reaction mixture was heated at 80 °C for an additional 48 h, eliminating the elements of CF_3SO_2H to produce the corresponding anil. Ethylenediamine (1.56 g, 0.026 mol) was added to the reaction and the mixture heated for an additional 24 h at 80 °C. The reaction mixture was added over a period of 1–2 h to a saturated solution of sodium hydroxide in methanol (250 mL) at 60 °C while O_2 was bubbled vigorously into the mixture. Oxygen sparging was continued for an additional hour. The reaction was poured into water and extracted with ether, and the ether extract was washed with 5% HCl. The acid wash was back-extracted with ether and the combined ether extracts were washed with a saturated sodium chloride solution. The ether extracts were dried (Na_2SO_4) and the solvent was removed in vacuo to leave an oil. Gas chromatographic analysis using authentic samples indicated a 64% yield of the desired pyrazine based on the starting α-bromo ketone. The product could be distilled at 90–92 °C (30 mmHg) [lit.[14] bp 74 °C (10 mmHg)]. The IR, NMR, and mass spectra were identical with those of a commercial sample.

2-Methyl-3-phenylpyrazine. The alkylation, elimination, ring condensation, and oxidation to the pyrazine were completed as described above, with the exception that THF was employed as the solvent. A sample of the alkylation product (92% yield) was isolated and found to be identical with a sample isolated in an earlier study. The crude material could be further purified by preparative thin-layer chromatography using 20 cm × 20 cm × 2000 μm silica gel plates, eluting with 5% ether in petroleum ether, or by preparative gas chromatography on a 4-mm i.d. × 5-ft glass column packed with 10% SF96 on Chromosorb WAW, DMCS. The yield of 2-methyl-3-phenylpyrazine by gas chromatography was 70% based on the starting bromo ketone: IR (neat) 3028, 1445, 1385, 1169, 1145, 1081, 1070, 1015, 754, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.44 (br s, 2), 7.50 (m, 5), 2.62 (s, 3); mass spectrum, m/e (rel intensity) 170 (66), 169 (100), 103 (45), 67 (25). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92. Found: C, 77.90; H, 6.00.

2-Methyl-3-octylpyrazine. The alkylation of *N*-phenyltriflamide (4.94 g, 0.022 mol) with 3-bromo-2-undecanone (5 g, 0.02 mol) and subsequent elimination of triflate were completed in one operation by using potassium carbonate (4.21 g, 0.030 mol) in refluxing THF. The alkylation product was identical with that synthesized previously.[10] The condensation of the imino ketone with ethylenediamine and oxidation of the resulting dihydropyrazine with O_2/NaOH/CH_3OH were carried out as described above. The crude product, 2-methyl-3-octylpyrazine, was recovered by preparative gas chromatography in 60% yield: IR (neat) 2927, 2852, 1454, 1402, 1164, 1031, 975, 846 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (br s, 2), 2.81 (t, 2, J = 7.6 Hz), 2.55 (s, 3), 1.30 (m, 12, CH_2's), 1.87 (t, 3, J = 5.6 Hz); mass spectrum, m/e (rel intensity) 207 (3, p + 1), 206 (2), 191 (3), 177 (2), 163 (3), 149 (2), 135 (5), 121 (12), 108 (100), 67 (3), 41 (5). Anal. Calcd for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75. Found: C, 75.64; H, 10.65.

2-*n*-Butyl-3-methylpyrazine (Isolation of Intermediate). *N*-Phenyltriflamide (3.6 g, 0.016 mol) was alkylated with 3-bromo-2-heptanone (2.9 g, 0.015 mol) by using potassium carbonate (2.03 g, 0.015 mol) in refluxing acetone for 36 h. The insoluble salts were filtered off, and the filtrate was concentrated to an oil and stirred in methylene chloride and potassium triflate

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filtered off. Removal of the solvent in vacuo left 4.49 g of an oil.

A sample (0.5 g) was taken up in THF (15 mL) and added to 10% HCl (20 mL). The resulting bright yellow mixture was extracted with pentane (4 × 5 mL) and the yield of 2,3-heptanedione was quantitated by gas chromatography (0.05 g). The pentane extract was then concentrated and the oil purified by preparative thin-layer chromatography (20 cm × 20 cm × 2000 μm, silica gel; 20% ether in petroleum ether), and 0.370 g of *N*-3-(2-oxoheptyl)-*N*-phenyltriflamide was isolated. The conversion from 3-bromo-2-heptanone was 23% to the anil and 64.4% to the substitution product or 87.4% overall. *N*-3-(2-Oxoheptyl)-*N*-phenyltriflamide was recrystallized from hexane: mp 55.5–58.5 °C; IR (KBr) 2961, 2938, 1722, 1361, 1224, 1210, 1185, 1145 cm^{-1}; NMR ($CDCl_3$) δ 7.30 (s, 5), 4.70 (t, 1, J = 7.4 Hz), 2.29 (s, 3), 1.39 (m, 6), 0.87 (t, 3, J = 5.2 Hz); mass spectrum, m/e (rel intensity) 337 (10), 294 (80), 161 (12), 132 (6), 120 (10), 119 (100), 118 (9), 104 (7), 77 (15). Anal. Calcd for $C_{14}H_{18}F_3NO_3S$: C, 49.84; H, 5.84. Found: C, 49.96; H, 5.45.

The product mixture (2.3 g) was refluxed in 25 mL of THF with potassium carbonate (0.7 g, 0.005 mol). After 18 h, GC/MS showed complete loss of the initial alkylation product with only elimination product remaining. An excess of ethylenediamine (0.82 g, 0.014 mol) was added and the mixture heated under reflux for 60 h. Gas chromatographic/mass spectroscopic analysis indicated aniline and the dihydropyrazine. This mixture was added to a solution of methanol saturated with sodium hydroxide. The solution was kept between 60 and 70 °C, and oxygen was added beneath the surface of the reaction throughout the 1.5 h required for the addition and the additional hour of heating. The reaction mixture was poured into water and extracted with pentane. The extracts were back-extracted with 5% HCl and a saturated salt solution and dried (Na_2SO_4). Concentration of the extracts followed by preparative GC produced the pyrazine in 65% yield. IR and mass spectra are identical with those previously described,[15] and the NMR spectrum is consistent with the structure: NMR ($CDCl_3$) δ 8.27 (s, 2), 2.82 (t, 2, J = 7.6 Hz), 2.57 (s, 3), 1.60 (m, 4), 0.95 (t, 3, J = 6.0 Hz).

Registry No. 2-Isobutyl-3-methylpyrazine, 13925-06-9; 2-methyl-3-phenylpyrazine, 29444-53-9; 2-methyl-3-octylpyrazine, 71700-39-5; 2-*n*-butyl-3-methylpyrazine, 15987-00-5; *N*-[3-(5-methyl-2-oxohexyl)]-*N*-phenyltriflamide, 71700-40-8; *N*-[3-(3-phenyl-2-oxopropyl)]-*N*-phenyltriflamide, 71700-41-9; *N*-[3-(2-oxoheptyl)]-*N*-phenyltriflamide, 71700-42-0; *N*-[3-(2-oxoheptyl)]aniline, 71700-43-1; 5-methyl-3-bromo-2-hexanone, 71700-44-2; 3-bromo-3-phenyl-2-propanone, 23022-83-5; 3-bromo-2-undecanone, 71700-45-3; 3-bromo-2-heptanone, 51134-59-9; *N*-phenyltriflamide, 456-64-4; ethylenediamine, 107-15-3.

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Application of *N*-Phenyltriflamide to the Synthesis of Deoxyaspergillic Acid

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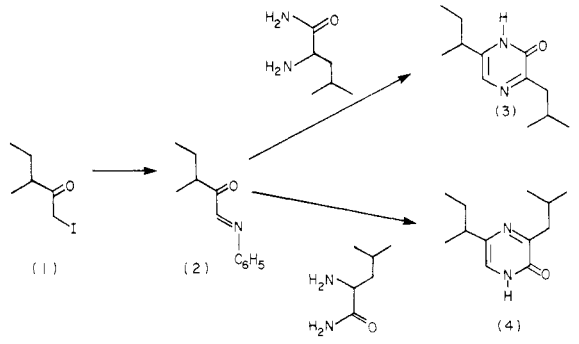
Because of its structural relationship to aspergillic acid, deoxyaspergillic acid (**3**, Scheme I) has long been of interest to both organic chemists and biochemists.[2-4] This 3,6-disubstituted 2-pyrazinone is a naturally occurring secondary metabolite produced by certain species of aspergillis[5] and streptomyces.[6,7] Early workers determined that when aspergillic acid was reduced with hydrazine, a single product, deoxyaspergillic acid, resulted.[2] In this paper, we focus on the development of an abbreviated synthesis of deoxyaspergillic acid employing the unique properties of *N*-phenyltriflamide in the preparation of the key intermediate, a primary α-imino ketone.[8-10] This investigation demonstrates not only the general utility of our recently developed pyrazine synthesis[8] but also the regioselectivity in the condensation of an α-keto amine with leucinamide.

Scheme I. Two Possible Condensation Modes[a] of α-Imino Ketone 2 with Leucinamide



[a] Even though both modes are possible, only deoxyaspergillic acid (3) was observed.

The synthetic concept is based on our earlier observation that imino ketones generated in situ from *N*-phenyltriflamide and the appropriate α-halo ketone can be smoothly condensed with 1,2-diamines to produce pyrazines.[8] The initial investigation focused on the condensation of symmetrical diamines with imino ketones while the present study is aimed at the regiospecific condensation of two unsymmetrical synthons, a keto imine (**2**) and leucinamide. Clearly, the leucinamide can add in two different directions to the imino ketone generating either the desired product (**3**) or compound **4** (Scheme I).

A review of the pertinent literature on pyrazinone syntheses revealed that early workers[11,12] found only the 3,5 isomers when condensing unsymmetrical dicarbonyls with α-aminoamides. However, recent workers[13] found that the product of the condensation of leucinamide and methylglyoxal was 33% 2-pyrazinone. Although the majority of the product was still 3,5 isomer, this encouraged us to consider the application of our pyrazine synthesis to the synthesis of deoxyaspergillic acid. Our imino ketone offered the additional advantage of two electrophilic centers with substantially different electronic properties.

The halo ketone (**1**) required for the synthesis of the

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