(t, J = 7.3 Hz, 2 H), 7.09–7.25 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.59, 21.92, 30.95, 32.87, 125.54, 126.36, 127.83, 129.77, 134.59, 139.41.

2-Hydroxyethyl *p*-tolyl sulfide, 27, was synthesized by a modified method of Nambara and Matsuhisa[42b] using sodium methoxide rather than KOH as the base. The product was obtained in 90% yield after purification on the chromatotron. ^{1}H NMR ($CDCl_3$) δ 2.1 (bt, 1 H), 2.33 (s, 3 H), 3.06 (t, J = 6.1 Hz, 2 H), 3.70 (dt, J = 4.9, 6.1 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.31 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.03, 38.10, 60.13, 129.85, 130.78, 131.12, 137.04.

2-Hydroxyethyl *p*-tolyl sulfoxide, 27SO,[48] was synthesized in 77% yield by treating **27** with 1 equiv of MCPBA in CH_2Cl_2 at −15 °C: ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.87–2.95 (m, 1 H), 3.07–3.15 (m, 1 H), 3.9–4.04 (m, 1 H), 4.13–4.24 (m, 2 H), 7.34 (d, J = 8.6 Hz, 2 H), 7.54 (d, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.31, 56.49, 59.00, 123.93, 130.01, 139.65, 141.64.

5-Hydroxypentyl *p*-tolyl sulfoxide, 29SO, was synthesized in 78% yield by treating **29** with 1 equiv of MCPBA in CH_2Cl_2 at −15 °C: ^{1}H NMR ($CDCl_3$) δ 1.4–1.85 (m, 6 H), 2.41 (s, 3 H), 2.54 (bs, 1 H), 2.75–2.86 (m, 2 H), 3.6 (t, J = 6.0 Hz, 2 H), 7.32 (d, J = 7.9 Hz, 2 H), 7.50 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.33 (q, J = 127 Hz), 21.93 (t, J = 129 Hz), 24.80 (t, J = 126 Hz), 32.02 (t, J = 126 Hz), 57.05 (t, J = 139 Hz), 61.97 (t, J = 141 Hz), 123.99 (d, J = 162 Hz), 129.86 (d, J = 161 Hz), 140.22 (s), 141.46 (s).

6-Hydroxyhexyl *p*-tolyl sulfoxide, 30SO, was synthesized in 94% yield by treating **30** with 1 equiv of MCPBA in CH_2Cl_2 at −15 °C: ^{1}H NMR ($CDCl_3$) δ 1.33–1.8 (m, 8 H), 2.2 (bs, 1 H), 2.41 (s, 3 H), 2.75–2.86 (m, 2 H), 3.6 (t, J = 6.0 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.36, 22.12, 25.29, 28.37, 32.32, 57.14, 62.52, 124.01, 129.87, 140.53, 141.38.

6-Hydroxyhexyl *p*-tolyl sulfone, 30SO$_2$: ^{1}H NMR ($CDCl_3$) δ 1.3–1.8 (m, 9 H), 2.46 (s, 3 H), 3.04–3.1 (m, 2 H), 3.61 (t, J = 6.4 Hz, 2 H), 7.36 (d, J = 8.1 Hz, 2 H), 7.78 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.60, 22.66, 25.18, 27.99, 32.20, 56.23, 62.56, 128.02, 129.86, 136.11, 144.60.

Total Rate Constant (k_T) Determination. The kinetic apparatus consists of a Spectra-Physics DCR11 Nd:YAG pulsed laser with second and third harmonic capability and a germanium diode detector and has previously been described in detail.[11,20]

Sample preparation was conducted by adding varying amounts of a stock solution of the substrate to a stock solution of oxygen saturated Rose Bengal. This method insured the same Rose Bengal concentration in each experiment. At least five pseudo-first-order rate constants were collected for each substrate. This experiment was repeated at least twice with fresh stock solutions.

Chemical Rate Constant (k_r) Determination. The chemical rate constants were determined using the method of Higgins, Foote, and Cheng.[55]

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Supplementary Material Available: Plots for the competitive determination of k_r for **6**, **10**, **19**, **23**, and **27–30** and ^{1}H NMR spectra of new compounds (50 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Cationic Carbon to Nitrogen Rearrangements in the Reactions of *N*-(Sulfonyloxy)amines with Aldehydes

Robert V. Hoffman* and James M. Salvador

Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003-0001

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A series of aromatic and aliphatic aldehydes was reacted with *N*-((*p*-nitrobenzenesulfonyl)oxy)methylamine in chloroform. Products resulting from both carbon migration and hydride migration to nitrogen were isolated. The ratios of carbon to hydride migration products were used to clarify the reaction mechanism. The results support a two-step process in which cationic carbon to nitrogen rearrangement is rate determining.

Introduction

We have previously reported that *N*-(sulfonyloxy)amines **1** add rapidly to oxonium ions **2** generated from ketones or ketone derivatives. The resulting tetrahedral intermediates **3** undergo rapid skeletal rearrangement by cationic carbon to nitrogen migration and yield rearranged amides **4** as products. The general process is summarized in Scheme I.[1]

The needed oxonium ions **2** can be generated by protonation of either enol ethers[2] or ketones[3] or by acid-catalyzed elimination in acetals.[4] The *N*-(sulfonyloxy)amines **1** are produced from the reaction of amines with sulfonyl peroxides.[5] While initial studies often utilized *N*-((*p*-nitrobenzenesulfonyl)oxy)methylamine (**1a**, R_1 = Me, Ar = *p*-$NO_2C_6H_4$), a variety of other *N*-(nosyloxy)amines were used subsequently. These experiments revealed that the addition of *N*-(nosyloxy)amines to oxonium ions, which produces the tetrahedral rearrangement precursor **3**, is sensitive to steric size in the *N*-(nosyloxy)amine **1** as well as to ring strain effects in cyclic oxonium ions **2**. Thus, best results were obtained when R_1 is methyl or a primary

Scheme I

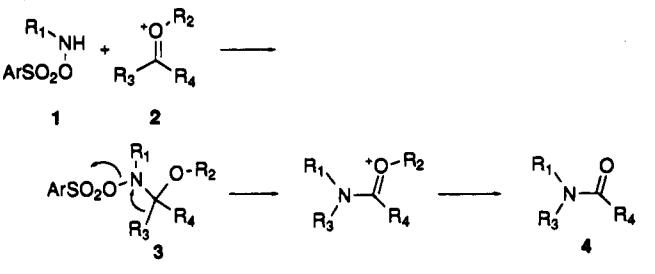

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Table I. Formation of *N*-Methyl-*N*-arylformamides 6 and *N*-Methylbenzamides 7 from the Reaction of YC_6H_4CHO 5 with *N*-(Sulfonyloxy)amine 1a in $CDCl_3$ at 25 °C

entry	aldehyde	yield (%) 6 + 7[a,b]	6/7[b]
1	5a, Y = *p*-OMe	96	23
2	5b, Y = *p*-Me	94 (74)	6.8 (7.2)
3	5c, Y = *p*-F	92 (58)	3.5 (3.7)
4	5d, Y = H	91 (72)	3.6 (4.4)
5	5e, Y = *p*-Br	82 (55)	2.0 (2.4)
6	5f, Y = 2,4,6-$(CH_3)_3$	100 (77)	1.2 (1.2)
7	5g, Y = 3,4-OCH_2O	88	48

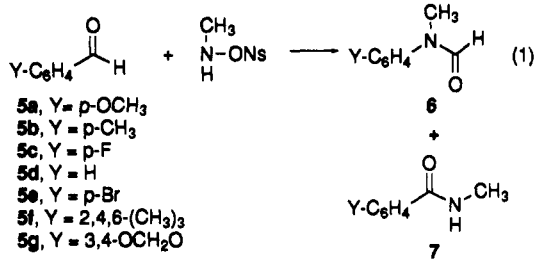
[a] Isolated yields of isomeric products based on starting aldehyde. [b] Data in parentheses are values obtained after separation of 6 and 7. All data are averages of two or more runs.

alkyl group, and yields decreased significantly if R_1 is a secondary alkyl group.[2,3] Ring strain in cyclic ketones increases the efficiency of the process markedly since formation of the tetrahedral adduct 3 relieves ring strain in the oxonium ion, and then ring expansion and consequent relief of ring strain drives the rearrangement.[3] Thus, best results were obtained for cyclobutanones and other strained cycloalkanones,[3] while poorest results were found for open-chain ketones.[6]

It was envisioned that aldehydes would be interesting substrates since (a) they are relatively unhindered and thus undergo carbonyl addition readily, (b) they would yield either amides by hydride rearrangement or formamides by carbon skeleton rearrangement and thus could be of preparative interest, and (c) the competition between hydride and carbon migration could provide insight into the electronic requirements of the carbon to nitrogen skeletal rearrangement.

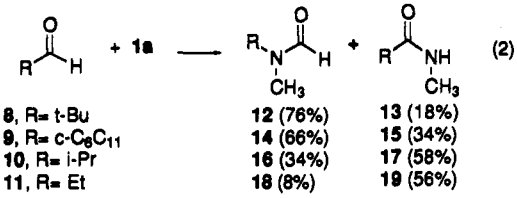
Results and Discussion

A series of substituted benzaldehydes 5a–g was reacted with 1a in chloroform-*d* (eq 1). The reaction was monitored by ^1H NMR by following the disappearance of both the aldehyde proton of 5 and the methyl signal (δ 2.8) of 1a. It was observed qualitatively that the presence of electron-donating groups on the aromatic ring increased the rate of conversion to products while electron-withdrawing groups slowed the reaction.[7] The products were isolated by bulb to bulb distillation, and the amount of *N*-methyl-*N*-arylformamide 6 (carbon migration product) and the amount of *N*-methylbenzamide 7 (hydride migration product) were determined by ^1H NMR of the product mixture. These products were separable by flash chromatography (ethyl acetate–hexane) for characterization and identification. The results are presented in Table I.



(1)

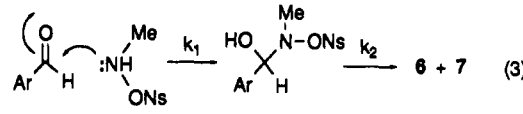
A series of aliphatic aldehydes 8–11 were also treated with 1a, and the formamide and amide products were quantitated by ^1H NMR or GC/MS of the product mixture (eq 2). In general, alkyl-group migration was not



(2)

favored over hydride migration to the extent seen for aromatic groups. Within the aliphatic series, however, migratory aptitudes were seen to decrease in the order *tert*-butyl (4.3) > cyclohexyl (1.9) > isopropyl (0.58) > ethyl (0.14).

The results presented above can be used to elucidate the mechanistic process involved in the reaction between aldehydes and *N*-(sulfonyloxy)amine 1a. It is assumed that the overall process involves two steps. The first is nucleophilic addition of 1a to the aldehyde to give a tetrahedral intermediate. The second is rearrangement of this intermediate to product (eq 3). The fact that methoxy-



(3)

substituted derivative 5a reacts appreciably faster than bromo compound 5e strongly suggests that the carbon-to-nitrogen rearrangement of the tetrahedral intermediate is the rate-determining step.

If nucleophilic addition were rate determining, an electron-withdrawing bromo substituent should render the carbonyl group more electrophilic and thus increase the rate of addition of 1a relative to an electron-donating methoxy substituent. On the other hand, if the second step (rearrangement of the tetrahedral intermediate) is rate determining, then the opposite behavior is predicted. The increased reactivity of *p*-methoxy compound 5a is consistent with the rearrangement step being rate determining.

Given that the rearrangement step is rate determining, the products 6 and 7 result from competing first-order rearrangements of the tetrahedral intermediate. A Hammett plot of log (6/7) product ratio of 5a–e in Table I versus the σ^+ constants for the corresponding substituents gave $\rho^+ = -1.11$ ($R = 0.995$). Poorer fits were found for other sets of substituent constants. Thus, electron-donating substituents result in an increased proportion of aryl rearrangement. The same trend is seen for alkyl group rearrangement in eq 2, in that more electron rich alkyl groups migrate more effectively.

Since a product ratio was used to determine ρ^+, the ρ^+ value actually corresponds to the difference in charge development on the aromatic ring when it is the migrating group, ρ^+_A, and when hydride is the migrating group and the aromatic moiety remains at the migration origin, ρ^+_H. Thus $\rho^+ = \rho^+_A - \rho^+_H$. The negative value of $\rho^+ = -1.11$ means that charge development on the ring during aryl migration is greater than when it remains at the migration origin during hydride migration. Furthermore, ρ^+_A is more negative than −1.11 indicating that appreciable positive charge is developed on the aromatic ring during migration and is comparable to cationic carbon to nitrogen migrations in *N*-(sulfonyloxy)tritylamines (Scheme II).[8] As Scheme

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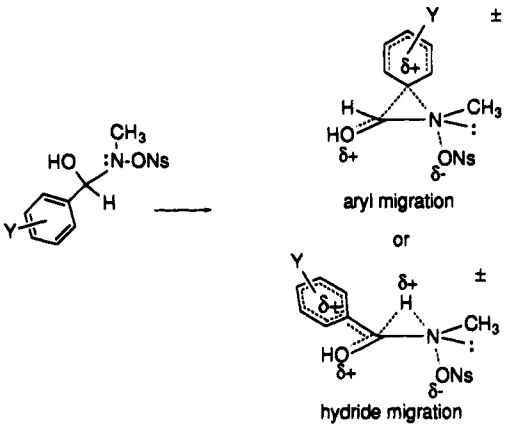
(7) For example, the reaction of *p*-methoxy compound 5a was complete in 1 h while *p*-bromo compound 5e required 6 h for complete reaction.

(8) Hoffman, R. V.; Poelker, D. J. *J. Org. Chem.* **1979**, *44*, 2364. The substituent influence on the formation of the tetrahedral intermediate is expected to be close to zero because it is an acid-catalyzed nucleophilic addition. Therefore, the ρ^+ values indicate substituent effects on the rearrangement step, not previous steps in the sequence.

Scheme II



II also shows, hydride migration results in less charge development on the aromatic ring because the lone pairs on the oxygen of the hydroxyl group efficiently stabilize developing charge at the migration origin and decrease the importance of aromatic stabilization and, hence, charge development.

The preference for aryl over hydride migration in the present study is not always observed in other cationic rearrangements. For example, the Baeyer–Villiger oxidation of benzaldehydes predominantly gives carboxylic acids by hydride migration when perbenzoic acid is the oxidant.[9] On the other hand, the use of monoperoxyphosphoric acid as the oxidant results in migratory aptitudes similar to those observed in the present rearrangement.[10] This is consistent with the notion that migratory aptitudes can be significantly influenced by the leaving ability of the leaving group.[8,11] The good leaving ability of the nosylate group thus contributes to the preference for aryl migration in the rearrangements of *N*-(nosyloxy)amines by ensuring an early transition state with low charge development at the migration origin.

A second and more important factor contributing to preferential carbon migration in the present systems is the hydroxyl group at the migration origin. We have previously shown that stabilization of positive charge at the migration origin is extremely important in determining migratory preferences in *N*-(sulfonyloxy)amine rearrangements.[12] Thus, in the rearrangements of *N*-((*m*-trifluoromethylbenzenesulfonyl)oxy)benzylamine and *N*-((*m*-trifluoromethylbenzenesulfonyl)oxy)benzhydrylamine, the Ph–H migration ratio changes from 4:56 in the former to 95:0 in the latter system. When groups are present to stabilize the developing charge at the migration origin, then the normally greater migratory aptitude of phenyl over hydrogen can be fully expressed. In the present case, the hydroxyl group at the migration origin is very effective at positive-charge stabilization, and thus the greater migratory aptitude of the phenyl group leads to its preferential rearrangement. That migratory preference can be lessened by attachment of electron-withdrawing substituents as seen in Table I.

The above results support the two-step process proposed in eq 3 with carbon to nitrogen rearrangement being rate determining. They also demonstrate the high propensity of *N*-(sulfonyloxy)amines to undergo rearrangements in the absence of base. Finally, the tetrahedral intermediate which undergoes rearrangement provides a mechanistic benchmark with which to compare other carbon to nitrogen rearrangements.

In both the Beckmann and Schmidt reactions, there has been some controversy over whether a trigonal or a tetrahedral intermediate is the principal rearranging species.[13] Based on the recent results of Aubé[14] and the results presented here, tetrahedral intermediates in both the Beckmann and Schmidt reactions can undergo facile rearrangement so they must be considered as possible reaction intermediates. Furthermore, these tetrahedral intermediates can now be generated and studied and the results compared with results obtained in systems where trigonal intermediates are the rearranging species.

Experimental Section

^{1}H NMR spectra were recorded at 200 MHz on a Varian instrument. Melting points are uncorrected. Thin-layer chromatography was performed on silica gel 60 F_{254} plates and visualized by UV irradiation and/or iodine. Flash chromatography was performed using silica gel 60 (230–400 mesh). GC/MS analyses were performed with phenylmethylsilicone or polyethylene glycol glass capillary columns (0.32-μm thickness) connected to a quadrupole mass detector. The column temperature was from 50 to 300 °C at 5 °C/min with 3 mL/min of helium gas flow rate. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ.

Reaction of *N*-Methyl-*N*-((*p*-nitrobenzenesulfonyl)oxy)amine (1a) with *p*-Methoxybenzaldehyde (5a). General Procedure. Aldehyde **5a** (122 μL, 137 mg, 1.0 mmol) was added to a solution of **1a** (0.28 g, 92% AO, 1.1 mmol) in chloroform-*d* (1.0 mL) in a 5-mm NMR tube, and the reaction was placed in a water bath at room temperature. After 1 h, ^{1}H NMR showed the disappearance of the methyl singlet of **1a** at δ 2.8. Triethylamine (0.3 mL, 2.2 mmol) was added, and the solvent was removed by rotary evaporation. Bulb to bulb distillation of the residue gave 151.7 mg (92%) of a 23:1 mixture of **6a** and **7a** by ^{1}H NMR. **6a**: ^{1}H NMR ($CDCl_3$) δ 3.27 (s, 3, CH_3N), 3.82 (s, 3, CH_3O, 6.94, 7.12 (AB q, 4, J = 9.1 Hz, Ar), 8.35 (s, q, *H*CO); IR (neat) 3040, 2040, 1670 (CO), 1510, 1245 cm^{-1}; mass spectrum *m/e* (rel intensity) 165 (72, P), 124 (59), 122 (100); n^{17} 1.5601 [lit.[15] n^{17} 1.5645]. Amide **7a** was not obtained in quantities sufficient for characterization but was quantitated from a small singlet at δ 3.02 which was assigned as the *N*-methyl group of **7a**.

In this example and others to follow, repetition of the experiment gave similar yields and product ratios.

Reaction of 1a with *p*-Methylbenzaldehyde (5b). By the same general procedure, **5b** (118 μL, 120 mg, 1.0 mmol) was reacted with **1a** (0.27 g 93% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 142.3 mg (96%) of a 6.8:1 mixture of **6b** and **7b** by ^{1}H NMR. Flash chromatography (ethyl acetate/hexane) separated the mixture into **6b** (97.3 mg, 0.653 mmol) and **7b** (13.6 mg, 0.091 mmol). **6b**: ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3, *p*-CH_3, 3.30 (s, 3, CH_3N), 7.07, 7.22 (AB q, 4, J = 8.3 Hz, Ar) 8.43 (s, 1, *H*CO); IR (neat) 3033, 1678 (CO) cm^{-1}; n^{20} 1.5521 [lit.[16] n^{20} 1.5504]; mass spectrum *m/e* (rel intensity) 149 (64, P), 120 (100). **7b**: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3, CH_3C), 3.01 (d, 3, J = 4.5 Hz, CH_3), 6.16, (b s, 1, N*H*), 7.12 (ABq, 4, J = 8.4 Hz, Ar); IR (neat) 2936, 1634 (CO), 1612 cm^{-1}; mp 141–147 °C [lit.[17] mp 145–147 °C]; mass spectrum *m/e*

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(rel intensity) 149 (27, P), 119 (100), 91 (59, C_7H_7), 65 (25).

Reaction 1a with *p*-Fluorobenzaldehyde (5c). By the same general procedure **5c** (107 μL, 124 mg, 1.0 mmol) was reacted with **1a** (270 mg, 93% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 139.5 mg (91%) of a 3.5:1 mixture of **6c** and **7c** by ^{1}H NMR. Flash chromatography (ethylacetate/hexane) was used to separate this mixture into **6c** (69.5 mg, 0.455 mmol) and **7c** (18.9 mg, 0.124 mmol). **6c**: ^{1}H NMR ($CHCl_3$) δ 3.30 (s, 3, CH_3N) 7.14 (d, 2, J = 7.62 Hz, 2-Ar), 7.15, (d, 2, J = 5.15 Hz, 3-Ar), 8.40 (s, 1, *H*CO); IR (neat) 3073, 2882, 1679 (CO) cm^{-1}; mp 45–48 °C; mass spectrum m/e (rel intensity) 153 (48, P), 124 (100, PCH_2O). Anal. Calcd for C_8H_8FNO: C, 62.74; H, 5.26; N, 9.15. Found: C, 62.76; H, 5.12; N, 8.96. **7c**: ^{1}H NMR ($CDCl_3$) δ 3.01 (d, 3, J = 4.8 Hz, CH_3N), 6.22 (b s, 1, N*H*), 7.11 (t, 2, J = 8.6 Hz, 2-Ar), 7.78 (dd, 2, J = 8.6, 5.3 Hz, 3-Ar) in good agreement with the literature spectrum;[17] IR (film) 1637 (CO); mp 127–131 °C [lit.[17] mp 131–132 °C]; mass spectrum m/e (rel intensity) 153 (23, P), 152 (23, PH, 123 (100, PCH_4N), 95 (61, C_6H_4F).

Reaction of 1a with Benzaldehyde (5d). Using the same general procedure, **5d** (102 μL, 106 mg, 1.0 mmol) was reacted with **1a** (270 mg, 94% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 130.6 mg (97%) of a 3.6:1 mixture of **6d** and **7d** by ^{1}H NMR. Flash chromatography (ethylacetate/hexane) was used to separate this mixture into **6d** (79.7 mg, 0.59 mmol) and **7d** (18.1 mg, 0.134 mmol). **6d**: ^{1}H NMR ($CDCl_3$) δ 3.33 (s, 3, CH_3N), 7.16–7.43 (m, 5, Ar), 8.49 (s, 1, *H*CO) in good agreement with the literature spectrum;[18] IR (neat) 2881, 1678 cm^{-1} which matched the literature spectrum;[19] mass spectrum m/e (rel intensity) 135 (67, P), 106 (100, PH_2O). **7d**: ^{1}H NMR ($CDCl_3$) δ 3.02 (d, 3, J = 4.8, CH_3) 6.28 (b s, 1, N*H*), 7.40–7.90 (m, 5, Ar) in good agreement with the literature spectrum;[20] IR (neat) 1637 cm^{-1} matched literature spectrum;[21] mp 78–80 °C [lit.[20] mp 76–78 °C]; mass spectrum m/e (rel intensity) 135 (33, P), 134 (34, PH), 105 (100, PCH_4N), 77 (81, C_6H_5).

Reaction of 1a with *p*-Bromobenzaldehyde (5e). Using the same general procedure **5e** (185.55 mg, 1.0 mmol) was reacted with **1a** (270 mg, 93% AO, 1.1 mmol). After 6 h, ^{1}H NMR showed that **1a** had disappeared. Bulb to bulb distillation gave 183.4 mg (86%) of a 2.0:1 mixture of **6e** and **7e** by ^{1}H NMR. Flash chromatography (ethyl acetate/hexane) was used to separate this mixture into **6e** (83.3 mg, 0.389 mmol) and **7e** (35.4 mg, 0.165 mmol). **6e**: ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 3, CH_3), 7.07, 7.54 (AB q, 4, J = 8.8 Hz, Ar), 8.47 (s, 1, *H*CO); IR (neat) 1675 cm^{-1}; mp 65–71 °C [lit.[22] mp 70–70.5 °C]; mass spectrum m/e (rel intensity) 215, 213 (66, 72, P), 186, 184 (88, 100, PCH_2O). **7e**: ^{1}H NMR ($CDCl_3$) δ 2.29 (d, 3, J = 4.6 Hz, CH_3), 6.46 (b s, 1, N*H*); 7.55, 7.65 (AB q, 4, J = 8.7 Hz, Ar); IR (neat) 1636 cm^{-1}; mp 165–168 °C [lit.[23] mp 165–167 °C]; mass spectrum m/e (rel intensity) 215, 213 (30, 32, P), 214, 212 (40, 43, PH), 185, 183 (96, 100, PCH_4N), 157, 155 (58, 52, C_6H_4Br), 76 (50), 75 (54), 74 (25), 50 (55).

Reaction of 1a with 2,4,6-Trimethylbenzaldehyde (5f). Using the same general procedure **5f** (147 μL, 148 mg, 1.0 mmol) was reacted with **1a** (270 mg, 93% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 176.8 mg (100%) of a 1.2:1 mixture of **6f** and **7f** by ^{1}H NMR. Flash chromatography (ethyl acetate/hexane) was used to separate this mixture into **6f** (74.0 mg, 0.418 mmol) and **7f** (62.4 mg, 0.353 mmol). **6f**: ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 6, 2,6-CH_3), 2.30 (s, 3,4-CH_3), 3.11 (s, 3, CH_3N), 6.95 (s, 2, Ar), 8.01 (s, 1, *H*CO); IR (neat) 2920, 1679 cm^{-1} which matches the literature spectrum;[24] mass spectrum, m/e (rel intensity) 177 (100, P), 160 (85). **7f**: ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 9, 2,4,6-CH_3) 2.99 (d, 3, J = 4.9, CH_3N), 5.68 (b s, 1, N*H*), 6.83 (s, 2, Ar); IR (neat) 1632 cm^{-1}; mp 154–157 °C; mass spectrum m/e (rel intensity) 177 (34, P), 147 (100, PCH_4N), 119, (40, C_9H_{11}). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.53; H, 8.51; N, 7.74.

Reaction of 1a with Piperonal (5g). Using the same general procedure **5g** (150.7 mg 1.0 mmol) was reacted with **2a** (270 mg, 93% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 158.8 mg (89%) of a 48:1 mixture (approximate) of **6g** and **7g** by ^{1}H NMR. **6g**: ^{1}H NMR ($CDCl_3$) δ 3.25 (s, 3 CH_3N) 6.02 (s, 2, CH_2), 6.61 (d, 1, J = 2.1 Hz, 2-C*H*), 6.67 (dd, 1, J = 9.1, 2.1 Hz, 6-C*H*), 6.82 (d, 1, J = 9.1, 5-C*H*), 8.34 (s, 1, *H*CO); IR (neat) 2900, 1673, 1228 cm^{-1}; mp 64–68 °C; mass spectrum m/e (rel intensity) 179 (100, P), 138 (63), 93 (61). Anal. Calcd for $C_{19}H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.58; H, 4.99; N, 7.70. Insufficient material was available to characterize **7g**.

Reaction of 1a with Trimethylacetaldehyde (8). Using the same general procedure, **8** (109 μL, 86 mg, 1.0 mmol) was reacted with **1a** (280 mg, 90% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 108.9 mg (95%) of a 4.3:1 mixture of **12** and **13** by ^{1}H NMR. These isomers were separated by flash chromatography (hexane–ethyl acetate). **12**: ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9, $(CH_3)_3C$), 2.87 (s, 3, CH_3N), 8.41 (s, 1, *H*CO) which matched the literature spectra;[25] mass spectrum m/e (rel intensity) 115 (33, P), 57 (100, C_4H_9). **13**: ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 9, $(CH_3)_3C$), 2.80 (d, 3, J = 4.7 Hz, CH_3N), NH not observed, which matched the literature spectra;[26] mass spectrum m/e (rel intensity) 115 (43, P), 100 (46, PCH_3) 72 (100).

Reaction of 1a with Cyclohexanecarboxaldehyde (9). Using the same general procedure, **9** (121 μL, 112 mg, 1.0 mmol) was reacted with **1a** (0.28 g, 90% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 140.1 mg (99%) of a 1.9:1 mixture of **14** and **15** by ^{1}H NMR. IR (mixture, neat) 1665 cm^{-1}. These isomers were separated by flash chromatography (hexane–ethyl acetate). **14**: ^{1}H NMR ($CDCl_3$) δ 1.0–2.0 (m, 10 $(CH_2)_5$), 2.81 (s, 3, CH_3N), 3.31 (m, 1, C*H*), 8.15 (s, 1, *H*CO) which matched the literature spectrum;[27] mass spectrum m/e (rel intensity) 141 (49, P), 98 (99), 60 (100). **15**: ^{1}H NMR ($CDCl_3$) δ 1.0–2.0 (m, 10, $(CH_2)_5$), 2.13 (m, 1, C*H*), 2.78 (d, 3, J = 4.8 Hz, CH_3N), 6.36 (b s, 1, N*H*) which matched the literature spectrum;[28] mass spectrum m/e (rel intensity) 141 (50, P), 86 (100), 83 (52), 73 (59), 58 (67), 55 (79).

Reaction of 1a with Isobutyraldehyde (10). Using the same general procedure, **10** (91 μL, 72 mg, 1.0 mmol) was reacted with **1a** (280 mg, 90% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 198.1 mg (97%) of a 1:1.7 mixture of **16** and **17** by ^{1}H NMR. IR (mixture, neat) 1655 cm^{-1}. These isomers were separated by flash chromatography (hexane–ethyl acetate). **16**: ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 6 H, J = 6.9 Hz, $(CH_3)_2C$), 2.79 (s, 3, CH_3N), 3.81 (sept, 1, J = 6.7, C*H*), 8.15 (s, 1, *H*CO) which matched the literature spectrum;[27] mass spectrum m/e (rel intensity) 101 (46, P), 86 (40, PCH_9), 58 (100). **17**: ^{1}H NMR ($CDCl_3$) δ 1.24 (d, 6, J = 6.8 Hz, $(CH_3)_2C$), 2.39 (sept, 1, J = 6.9 Hz, C*H*), 2.80 (d, 3, J = 6.0, CH_3N), 6.13 (br s, 1 N*H*) which matched literature data;[29,30] mass spectrum m/e (rel intensity) 101 (22, P), 58 (100).

Reaction of 1a with Propanal (11). Using the same general procedure, freshly distilled **11** (72 μL, 58 mg, 1.0 mmol) was reacted with **1a** (320 mg, 81% AO, 1.1 mmol) for 6 h. Bulb to bulb distillation gave 58.0 mg (67%) of a 1:7 mixture of **18** and **19** by ^{1}H NMR: IR (mixture, neat) 1653 cm^{-1}. **18**: ^{1}H NMR ($CDCl_3$) δ CH_3C (overlapped by isomer **19**) 2.87, 2.95 (2s, 3 H total, CH_3N rotamers), 3.32, 3.39 (2q, J = 7.2 Hz, CH_2 rotamers, 8.03, 8.10 (2 s, *H*CO rotamers) which matched the literature spectrum;[27] mass spectrum m/e (rel intensity) 87 (58), 58 (100). **19**: ^{1}H NMR matched spectrum of authentic sample (Aldrich); mass spectrum m/e (rel intensity) 87 (100), 72 (40), 58 (31).

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