mixture, mp 197 °C, to give a product identical with that obtained above.

Silver(I) Oxide Oxidation of 3a to 2. The compound **3a** (10 mg, 0.036 mmol) was dissolved in ethyl acetate (3 mL) and stirred vigorously with silver(I) oxide (10 mg) in the presence of anhydrous Na_2SO_4 (10 mg) at room temperature. The reaction mixture turned yellow immediately, and after 15 min of stirring it was filtered. Removal of the solvent from the filterate under vacuum gave the crude quinone **2**, which was recrystallized from a dichloromethane–hexane mixture to furnish **2** (10 mg, 100%), identical with that obtained above.

Acetylation of 3a. The compound **3a** (100 mg, 0.36 mmol) was treated with a mixture of dry pyridine (0.5 mL) and acetic anhydride (2 mL). The reaction mixture was stirred at ambient temperature for 10 h and then poured into cold water (10 mL). The aqueous layer was extracted thoroughly with ether (3 × 20 mL), and the combined ethereal layer was washed with 10% HCl (10 mL), water (10 mL), and finally with brine (15 mL). Drying over anhydrous Na_2SO_4, removal of solvent, and recrystallization of the crude product from dichloromethane–hexane mixture gave the white crystalline pure diacetate **3b** (121 mg, 98%): mp 245 °C; IR (KBr) 1750, 1640, 1165, 880 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.20–7.0 (m, 1 H), 6.76 (br s, 3 H), 6.64–6.40 (m, 1 H), 5.20 (dd, $J_1 = J_2 = 4$ Hz, 1 H), 4.76–4.56 (m, 1 H), 4.26 (br t, 1 H), 3.8 (br s, 2 H), 2.40 (s, 6 H), 2.20 (br s, 2 H). Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.90; H, 5.01. Found: C, 72.86; H, 4.98.

Hydrogenation of the Diacetate 3b. The diacetate **3b** (17 mg, 0.049 mmol) was dissolved in ethyl acetate and hydrogenated over 10% palladium–carbon for 1 h. The catalyst was filtered, and the solvent was removed under vacuum. The crude product was recrystallized from a dichloromethane–hexane mixture to furnish the hydrogenated product **16** (17 mg, 94%): mp 195 °C; IR (KBr) 1750, 1700, 1180, 880 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 3.68–3.48 (m, 1 H), 3.32 (br s, 3 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 2.0–1.16 (m, 14 H). Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.71; H, 6.56. Found: C, 71.84; H, 6.60.

Acetylation of the Lactone 4a. The lactone **4a** (100 mg, 0.36 mmol) was dissolved in dry pyridine (0.5 mL) and acetic anhydride (2 mL) and left aside overnight. The reaction mixture was poured into cold water (15 mL), and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with 10% HCl (10 mL), water (10 mL), and finally with brine (15 mL). The ether extract was dried over anhydrous Na_2SO_4, and solvent was removed to give the crude acetate. It was recrystallized from a dichloromethane–hexane mixture to obtain the yellow crystalline acetate **4b** (113 mg, 99%): mp 155 °C; IR (KBr) 1745, 1700, 1180, 820 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.72 (dd, $J_1 = 6$ Hz, $J_2 = 4$ Hz, 1 H), 7.4–7.2 (m, 2 H), 7.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 6.8 (dd, $J_1 = J_2 = 2$ Hz, 2 H), 6.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 4.45 (br s, 1 H), 3.94 (br s, 1 H), 2.48 (s, 3 H), 2.25 (br s, 2 H); ^{13}C NMR (25.0 MHz, $CDCl_3$) δ 169.0, 162.7, 146.3, 142.5, 142.0, 141.5, 140.1, 135.8, 133.1, 129.7, 128.0, 125.8, 125.1, 118.6, 65.5, 47.8, 47.4, 20.5. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.54; H, 4.40.

Reaction between 1,2,3,4-Tetrahydro-1,4-methanonaphthalene-5,8-dione (11) and Tropone. The mixture of dihydroquinone **11** (570 mg, 3.3 mmol) and tropone (420 mg, 4.0 mmol) in 15 mL of xylene was heated at 140 °C for 26 h under nitrogen atmosphere. The solvent was distilled off under reduced pressure, and the residue was chromatographed on a silica gel (20 g) column. After a forerun of the unreacted quinone **11** (300 mg), elution of the column with a 15% ethyl acetate–hexane mixture gave **12** (40 mg, 19.3%), **14** (10 mg, 4.8%), **13a** (115 mg, 55.5%), and quinol **15** (70 mg, mp 190 °C). Compound **12** was recrystallized from a dichloromethane–hexane mixture to furnish yellow crystals: mp 195 °C; IR (KBr) 1640, 1580, 1320, 860 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.20–7.00 (m, 1 H), 6.82 (t, 1 H), 6.52 (t, 1 H), 5.24 (br d, $J = 12$ Hz, 1 H), 5.08–4.88 (m, 1 H), 4.76–4.44 (m, 1 H), 3.48 (br s, 2 H), 2.08–1.08 (m, 6 H); mass spectrum, m/z 278.0 (M^+). Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.69; H, 4.98. Compound **14** was recrystallized from a dichloromethane–hexane mixture to furnish red crystals: mp 210 °C; IR (KBr) 3250, 2650, 2580, 830 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 8.18 (t, $J = 6$ Hz, 1 H), 7.40–7.16 (m, 2 H), 7.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 6.02 (d, $^1/_2$ AB, $J = 12$ Hz, 1 H), 5.42 (br s, 1 H), 3.90 (br s, 1 H), 3.60 (br s, 1 H), 2.10–1.24 (m, 6 H); mass spectrum, m/z 278.0 (M^+). Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.83; H, 5.00. Compound **13a** was recrystallized from ethyl acetate: mp 264 °C; IR (KBr) 3250, 1640, 1620, 1300, 840 cm^{-1}. This compound was best characterized as its diacetate **13b** (vide infra).

Acetylation of 13a. The compound **13a** (100 mg, 0.36 mmol) was treated with a mixture of dry pyridine (0.5 mL) and acetic anhydride (2 mL). The reaction mixture was stirred at ambient temperature for 12 h and then poured into cold water (10 mL). The aqueous layer was extracted with ether (3 × 20 mL). The combined ethereal layer was washed with 10% HCl (10 mL), water (10 mL), and finally with brine (15 mL). Drying over anhydrous Na_2SO_4, removal of solvent, and recrystallization of the crude product from a dichloromethane–hexane mixture furnished the pure diacetate **13b** (127 mg, 98.5%): mp 220 °C; IR (KBr) 1760, 1670, 1180, 890 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 7.22–7.0 (m, 1 H), 6.88 (br t, 1 H), 6.76 (br t, 1 H), 5.24 (br d, $J = 12$ Hz, 1 H), 4.68 (br d, $J = 8$ Hz, 1 H), 4.30 (br t, 1 H), 3.28 (br s, 2 H), 2.40 (s, 6 H), 2.0–1.10 (m, 6 H). Anal. Calcd for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53. Found: C, 72.26; H, 5.41.

Hydrogenation of the Diacetate 13b. The diacetate **13b** (16 mg, 0.044 mmol) was dissolved in ethyl acetate (2 mL) and hydrogenated over 10% palladium–carbon catalyst for 1 h. The catalyst was filtered, and the solvent was removed under reduced pressure to yield the crude product. This was recrystallized from a dichloromethane–hexane mixture to furnish **16** (15 mg, 94%), identical with the sample prepared above through hydrogenatiion of the diacetate **3b**.

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Registry No. 1, 6829-72-7; 2, 119973-17-0; **3a**, 119973-18-1; **3b**, 119973-20-5; **4a**, 119973-19-2; **4b**, 119973-21-6; 5, 3090-47-9; 11, 61632-88-0; 12, 119973-22-7; **13a**, 119973-23-8; **13b**, 119973-26-1; 14, 119973-24-9; 15, 16144-91-5; 16, 119973-25-0; tropone, 539-80-0.

Formation of Thiocarbamates in the Oxidative Condensation of Amines and Organic *N*-Chloroamines with Potassium Ethyl Xanthate

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Introduction

We have been investigating new reactions of organic *N*-chloroamines in an effort to develop methods of derivatizing them for analysis in dilute aqueous solution. In a series of papers Smith et al.[1-4] reported that the sulfur moiety of certain thiols, dithiocarbamates, and carbodithioates reacted with organic *N*-chloroamines or with amines in the presence of iodine to form sulfenamide products. Although he examined the reaction of xanthate salts with chloroamines, he failed to characterize the products beyond their inability to accelerate rubber vulcanization. When we reacted *N*-chloropiperidine with the sodium salt of xanthic acid, we expected a sulfenamide product to form. Instead we isolated a thiocarbamate. Subsequently we noted that in a recent patent Giancarlo[5]

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Table I

precursor	oxidant	product	% isolated yield
aniline	I_2	phenylcarbamothioic acid, ethyl ester	82
methylamine	I_2	methylcarbamothioic acid, ethyl ester	64
	ClO^-	methylcarbamothioic acid, ethyl ester	56
N-chloro-*N*-methylamine		methylcarbamothioic acid, ethyl ester	83
dimethylamine	I_2	dimethylcarbamothioic acid, ethyl ester	93
	ClO^-	dimethylcarbamothoic acid, ethyl ester	31
isobutylamine	I_2	isobutylcarbamothioic acid, ethyl ester	91
pyrrolidine	I_2	1-pyrrolidinecarbothioic acid, ethyl ester	100
	ClO^-	1-pyrrolidinecarbothioic acid, ethyl ester	32
piperidine	I_2	1-piperidinecarbothioic acid, ethyl ester	91
	ClO^-	1-piperidinecarbothoic acid, ethyl ester	72
N-chloropiperidine		1-piperidinecarbothioic acid, ethyl ester	24
allylamine	I_2	allylcarbamothioic acid, ethyl ester	94

reported the formation of thiocarbamates on reaction of potassium ethyl xanthate with amines in water in the presence of an oxidizer such as sodium hypochlorite. Since this reaction is a very simple and convenient method of preparing thiocarbamates in high yields and because this work has not been previously described in detail in the refereed literature, we report our findings, which elucidate and complement those of Giancarlo.

Results and Discussion

In Table I are listed the compounds synthesized and the yields observed for the different methods (eq 1 and 2). In

$$R_2NCl + CH_3CH_2OC(S)S^- \rightarrow CH_3CH_2OC(S)NR_2 \quad (1)$$

$$R_2NH + CH_3CH_2OC(S)S^- \xrightarrow[NaOCl]{KI_3\ or} CH_3CH_2OC(S)NR_2 \quad (2)$$

general, the yields and the purity of the distilled products were highest when potassium triiodide was used as the oxidant and somewhat lower when sodium hypochlorite was added to a mixture of the amine and xanthate. When a chloroamine was reacted directly with potassium ethyl xanthate, the yields varied. *N*-Chloro-*N*-methylamine gave the highest yield of the corresponding thiocarbamate, but the less water-soluble *N*-chloropiperidine gave a lower yield of thiocarbamate than when iodine was used. The yields of thiocarbamates were highest when the reaction was conducted at pH >11 and in the presence of excess amine. Similar conditions were found to be optimum in analogous syntheses of thioamides from carbidithioates and in the reactions reported by Giancarlo.[5] Aniline gave a quantitative yield of crude product, which after recrystallization gave an 82% yield of pure compound. In an attempt to synthesize a thiocarbamate from a less water-soluble aromatic amine (*p*-chloroaniline), ethanol was added as a cosolvent in order to solubilize the amine. However, only a crude product was isolated in less than 10% yield. No attempt was made to optimize the yield.

The formation of elemental sulfur was observed when triiodide was used, less was observed when the organic chloroamine was used, but none appeared to be present when hypochlorite was used. A similar loss of sulfur has been observed in the reaction of sodium carbodithioates with chloroamines[3] or in the oxidative condensation of amines with carbodithioate or trithiocarbonate in the presence of iodine[3] and also in the formation of thioureas from tetrahydro-1,2,5-thiadiazines.[4] Alliger et al.[3] suggested that the initial products of these reactions were sulfenamides, which decomposed with loss of sulfur because of their instability. Thiocarbamates are most frequently prepared by three methods: the reaction of alkoxides with isothiocyanates, the reaction of amines with carbonochloridothioic acid *O*-alkyl esters, and the reaction of thiocarbamoyl chlorides with alcohols. However, the desired isothiocyanate, carbonochloridothioic acid, or thiocarbamoyl chloride are not always readily available. The oxidative condensation of amines with xanthates in the presence of potassium triiodide provides a convenient mild method for the synthesis of thiocarbamates from simple precursors in high yield and purity. Since xanthates can easily be synthesized in situ by the reaction of alcoholates with carbon disulfide, thiocarbamates of varying structure can be prepared in one-pot reactions from alcohols and amines.

Experimental Section

Materials. For all the syntheses, *O*-ethylxanthic acid, potassium salt (Aldrich Chemical Co., Milwaukee, WI), was used. A commercial solution of sodium hypochlorite (Clorox) was standardized by iodimetric titration prior to use. Anhydrous ethyl ether and acetonitrile (EM Science, Cherry Hill, NJ) were used as received. Piperidine, aniline, dimethylamine hydrochloride, and methylamine hydrochloride were used as received from commercial sources. Pyrrolidine and isobutylamine were also available commercially and were distilled before they were used. A working solution of potassium triiodide was prepared by mixing iodine (62.5 g, 246 mmol) in 400 mL of deionized water containing potassium iodide (49.8 g, 300 mmol). The mixture was warmed to maximize dissolution of the iodine, cooled, filtered, and standardized. Solutions of organic *N*-chloroamines were prepared by slowly adding 1 equiv of aqueous chlorine to 3 equiv of the organic amine.

Analyses. Approximately 2 g of potassium iodide was dissolved in 100 mL of deionized water containing 5.0 mL of glacial acetic acid. Using a micropipette, 0.500 mL of NaOCl or KI_3 solution was added to the flask. The solution was titrated with standardized 0.1 N sodium thiosulfate.[6]

General. Purity of reaction products was checked by gas chromatography (flame ionization detector) by using a Hewlett-Packard Model 5890A in the purged splitless mode. A 0.32 mm i.d. × 30 m SPB-5 fused silica capillary GC column with a 0.25 μm film thickness (Supelco, Inc., Bellefonte, PA) was used. After a splitless injection for 2.00 min, purge was applied. After an initial temperature hold of 1 min at 100 °C, the column was temperature programmed at 10 °C/min to a final temperature of 250 °C and maintained at this temperature for 10 min.

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Chromatograms were recorded on a Hewlett-Packard Model 3393A recorder-integrator. Infrared spectra were recorded on a Beckman Microlab 620MX computing infrared spectrophotometer, and nuclear magnetic resonance (NMR) spectra were recorded with a JEOL FX 90Q Fourier transform NMR spectrometer using deuteriobenzene or deuterioacetone as solvents. Benzene (C_6D_5H) or acetone (C_3D_5H) was used as the internal standard.

Synthesis. Method A. In a typical procedure *O*-ethylxanthic acid, potassium salt (7.05 g, 44 mmol), and the amine (100 mmol) were dissolved in 100 mL of deionized water in a 500-mL Erlenmeyer flask. When an amine hydrochloride was used, the pH of the solution was first adjusted to >11 with 10 N NaOH. The flask was immersed in an ice bath, and potassium triiodide (103.6 mL of a 0.38 M solution (40 mmol) freshly standardized with sodium thiosulfate[6]) was added dropwise with magnetic stirring over 20–30 min. A yellow milky suspension was formed. Once the addition of potassium triiodide was completed, the mixture was stirred for another 30 min to complete the reaction. The yellow organic layer was then extracted with anhydrous ether three times. The ether layer was dried with anhydrous sodium sulfate, and the solution was concentrated on a rotary evaporator. The yellowish oil contained yellow crystals, which, by their solubility, melting point (112–114 °C), and ignition, appeared to be sulfur. The oil was removed and purified by a simple vacuum distillation. The purity of the compounds was generally greater than 98%. The identity of the products was confirmed by their melting points, boiling points (where possible), elemental analysis (percent compositions of C, H, N, and S were within 0.3% of theoretical values), and NMR and IR spectral data. All compounds showed C=S stretching vibrations between 1520 and 1552 cm^{-1}.

Method B. Thiocarbamates were also prepared by reacting the chloroamine with potassium ethyl xanthate. The chloroamine was prepared by the dropwise addition of a standardized solution of sodium hypochlorite (40 mmol) to 100 mL of an aqueous solution of the amine (100 mmol). The resulting oily suspension was added to 100 mL of an aqueous solution containing 44 mmol of potassium ethyl xanthate.

Method C. Thiocarbamates were prepared by the dropwise addition of a standardized solution of sodium hypochlorite (40 mmol) to 100 mL of an aqueous solution containing amine (100 mL) and potassium ethyl xanthate (44 mmol).

Methylcarbamothioic acid *O*-ethyl ester: bp 60–62 °C (1.4 mmHg) [lit.[7] bp 93 °C (10 mmHg)]; ^1H NMR (C_6D_6) δ 7.5–5.5 (2 broad m, 1 H, NH), 4.37 (q, 2 H, CH_2), 2.44 (d of d, 3 H, NCH_3), 1.02 (t, 3 H, CH_3); IR (film) 3280, 2985, 1537, 1365, 1221, 1056 cm^{-1}. Anal. Calcd for C_4H_9NOS: C, 40.30; H, 7.63; N, 11.75; S, 26.90. Found: C, 40.43; H, 7.69; N, 11.69; S, 26.75.

Dimethylcarbamothioic acid *O*-ethyl ester: bp 88–89 °C (12 mmHg) [lit.[8] bp 81–82 °C (10 mmHg)]; ^1H NMR (C_6D_6) δ 4.40 (q, 2 H, OCH_2), 3.0 (s, 3 H, NCH_3) 2.55 (s, 3 H, NCH_3) 1.03 (t, 3 H, CH_3); IR (film) 1525, 1398, 1292, 1195, 1038 cm^{-1}. Anal. Calcd for $C_5H_{11}NOS$: C, 45.08; H, 8.32; N, 10.52; S, 24.07. Found: C, 44.79; H, 8.25; N, 10.38; S, 23.83.

Isobutylcarbamothioic acid *O*-ethyl ester: bp 78–80 °C (1.4 mmHg); ^1H NMR (C_6D_6) δ 7.79 (broad s, 0.4 H, NH), 6.22 (broad s, 0.6 H, NH), 4.40 (d of q, 2 H, OCH_2) 3.21 (t, 1.2 H, NCH_2) 2.80 (t, 0.8 H, NCH_2) 1.65 (m, 1 H), 1.05 (d of t, 3 H), 0.67 (d, 6 H); IR (film) 3250, 2960, 1525, 1200 cm^{-1}. Anal. Calcd for $C_7H_{15}NOS$: C, 52.13; H, 9.38; N, 8.69; S, 19.88. Found: C, 52.02; H, 9.41; N, 8.65; S, 19.79.

Phenylcarbamothioic acid *O*-ethyl ester: recrystallized from ethanol; mp 66.5–67.5 °C (lit.[9] mp 68–70 °C); ^1H NMR (C_6D_6) δ 8.4 (broad s, 1 H, NH), 6.7–7.2 (m, 5 H, aromatic), 4.33 (q, 2 H, CH_2O), 0.96 (t, 3 H, CH_3); IR (KBr) 3223, 1600, 1552, 1499, 1409, 1377, 1335, 1200, 1040 cm^{-1}.

1-Pyrrolidinecarbothioic acid *O*-ethyl ester: bp 91–92 °C (1.5 mmHg) [lit.[10] bp 141 °C (17.5 mmHg)]; ^1H NMR (C_6D_6) δ 4.5 (q, 2 H, CH_2O), 3.57 (broad t, 2 H, ring), 3.07 (broad t, 2 H, ring), 1.4–0.93 (m, 7 H); IR (film) 1495, 1474, 1455, 1260, 1223, 1046 cm^{-1}. Anal. Calcd for $C_7H_{13}NOS$: C, 52.79; H, 8.23; N, 8.80; S, 20.13. Found: C, 52.56; H, 8.26; N, 8.72; S, 20.03.

1-Piperidinecarbothioic acid *O*-ethyl ester: bp 91–92 °C (1.4 mmHg) [lit.[10] bp 147.9 °C (25 mmHg)]; ^1H NMR (C_6D_6) δ 4.47 (q, 2 H, OCH_2), 3.86 (m, 2 H, ring), 3.27 (m, 2 H, ring), 2.24 (m, 6 H), 1.15 (t, 3 H, CH_3); IR (film) 1492, 1443, 1292, 1268, 1243, 1190 cm^{-1}. Anal. Calcd for $C_8H_{15}NOS$: C, 55.45; H, 8.73; N, 8.08; S, 18.50. Found: C, 55.37; H, 8.77; N, 8.06; S, 18.42.

Allylcarbamothioic acid *O*-ethyl ester: bp 71–73 °C (1.0 mmHg) [lit.[11] bp 64–65 °C (0.3 mmHg)]; ^1H NMR (C_6D_6) δ 7.7 (broad m, $^1/_3$ NH), 6.7 (broad m, $^2/_3$ NH), 5.6 (m, 1 H, vinylic), 4.95 (d of d, 2 H, vinylic), 4.32 (q, 2 H, OCH_2), 3.95 (broad s, 1.3 H, allylic), 3.55 (broad s, 0.7 H, allylic), 1.06 (t, 3 H, CH_3); IR (film) 3250, 1520, 1393, 1324, 1270, 1193 cm^{-1}.

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Registry No. *O*-Ethylxanthic acid, potassium salt, 140-89-6; methylcarbamothioic acid *O*-ethyl ester, 817-73-2; dimethylcarbamothioic acid *O*-ethyl ester, 17996-38-2; isobutylcarbamothioic acid *O*-ethyl ester, 82360-11-0; phenylcarbamothioic acid *O*-ethyl ester, 3111-89-5; 1-pyrrolidinecarbothioic acid *O*-ethyl ester, 56525-82-7; 1-piperidinecarbothioic acid *O*-ethyl ester, 56525-81-6; allylcarbamothioic acid *O*-ethyl ester, 817-97-0; aniline, 62-53-3; methylamine, 74-89-5; *N*-chloro-*N*-methylamine, 6154-14-9; dimethylamine, 124-40-3; isobutylamine, 78-81-9; pyrrolidine, 123-75-1; piperidine, 110-89-4; *N*-chloropiperidine, 2156-71-0; allylamine, 107-11-9.

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On the Relative Energies of ab Initio Structures of *N*-Methylformamide Anions and Their Lithium Derivatives. An Estimate of the Magnitude of Chelate Stabilization

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The term "dipole-stabilized anion" was coined by Beak to describe the situation that results when a carbanion is stabilized by an adjacent dipole.[1] Such a situation arises when, for example, an amide is deprotonated α to nitrogen.[2] The simplest model for such a system is *N*-methylformamide anion: $HCONHCH_2^-$. In 1981, a collaborative effort from Houk, Beak, and Schleyer compared the relative energies of several dipole-stabilized anions with non-dipole-stabilized analogues.[3] For *N*-methylformamide anion, the effect of dipole stabilization was demonstrated by comparing the proton affinities of $HCONHCH_2^-$ and $NH_2CH_2^-$. Single-point calculations using the 4-31+G basis set on STO-3G optimized geometries showed that formylating the nitrogen of $NH_2CH_2^-$ provided 28 kcal/mol stabilization.

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