$J_{C1/H1}$ = 163 Hz; field desorption mass spectrum, m/e_{calcd} 952, m/e_{found} 952 (M^+). Anal. Calcd for $C_{51}H_{61}N_5O_{13}\cdot 0.5H_2O$: C, 63.14; H, 6.54; N, 7.22. Found: C, 63.21; H, 6.34; N, 7.26.

Registry No. **1**, 1145-80-8; **2**, 106-95-6; **3**, 88295-41-4; **4**, 88224-11-7; **5**, 117710-12-0; α-**6**, 20787-16-0; β-**6**, 77943-32-9; **7**, 83441-63-8; **8a**, 88287-93-8; **8b**, 88287-92-7; **9**, 67817-37-2; **10a**, 118417-95-1; **10b**, 118417-98-4; **11a**, 118417-76-8; **11b**, 118490-32-7; **12**, 672-66-2; **13**, 118398-50-8; **14**, 118417-77-9; **15**, 118417-96-2; **16**, 118417-78-0; **17**, 88287-94-9; **18**, 118398-51-9; **19**, 118417-79-1; **20**, 88287-95-0; **21**, 88287-96-1; **22**, 88224-21-9; **23**, 118398-52-0; **24**, 118398-53-1; **25**, 118398-54-2; **26**, 118398-55-3; **27**, 118417-97-3; **28**, 118398-56-4; **29**, 118398-57-5; **30**, 88287-97-2; **31**, 118398-58-6; **32**, 88287-99-4; **33**, 118398-59-7.

S_NAr, S_N2, and Aromatic Addition Processes in the Reactions of Picryl Ethers with Nitrogen and Carbon Bases

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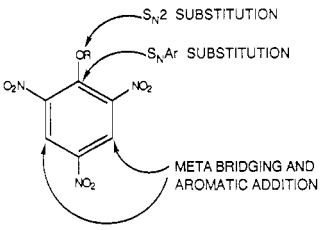
The reactions of methyl, cyclohexyl, and phenyl picryl ethers with diethyl- and triethylamine in chloroform, acetone, and 1,3-dicarbomethoxyacetone have been studied. A number of different processes were observed, depending on substrate structure. Both amine nitrogen and enolate carbon act as nucleophiles in these reactions. With unhindered picryl ethers like 2,4,6-trinitroanisole, dealkylation often occurs via S_N2 attack on the methyl group. With more hindered picryl ethers, addition to the ring is more common, resulting in covalent σ complexes, substituted picramides, or bicyclo [3.3.1] nitropropenenitronates. In this paper, structural features that influence reaction path are discussed.

Introduction

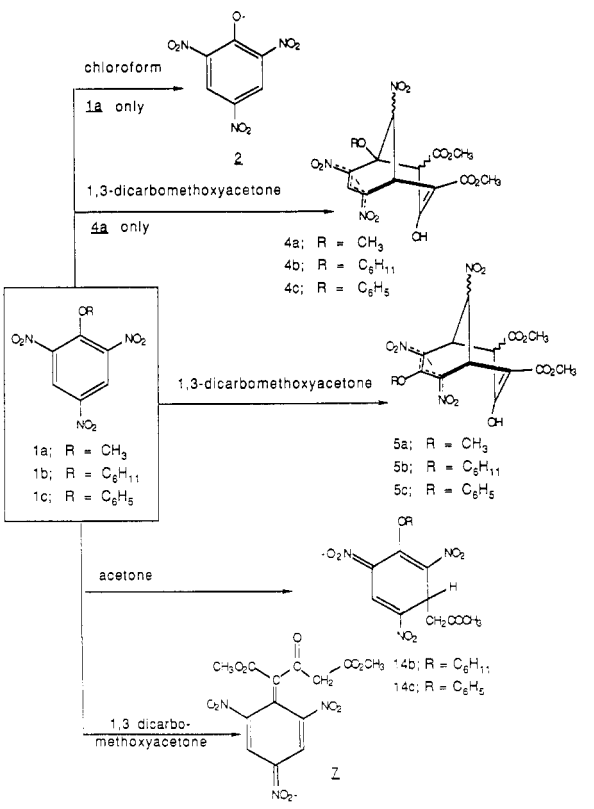
While there has been much interest in the reactions of picryl ethers and related compounds with oxygen nucleophiles,[1-4] the behavior of these aromatics with carbon and nitrogen nucleophiles has been less well studied. Because of the multiplicity of reaction sites in compounds like 2,4,6-trinitroanisole (TNA), **1a**, we were prompted to more fully characterize the alternative substitution and addition processes that this compound and similar picryl ethers can undergo.



Different substitution and addition reactions occur with different aromatic substrates $(O_2N)_3C_6H_2OR$ (R = CH_3, C_6H_{11}, C_6H_5) and nucleophiles (enolate or amine). Analysis of the results provides a clearer picture of the processes that occur with this interesting type of electron-deficient aromatic. A summary of possible products is shown in Schemes I and II. These are formed from secondary and tertiary amines in ketonic and nonketonic solvents. With tertiary amines dealkylation often occurs in nonacidic solvents, whereas in acidic solvents proton abstraction is sometimes followed by lyate attack on the aromatic substrate.

The reactions of picryl ethers in solution of amines and carbon acids are complex.[4-6] It is therefore important to understand the behavior of these aromatic substrates with amines in nonketonic solvents. Early work by Servis[5] and Clapp[6] on the reactions of TNA and other more hindered picryl ethers with primary amines is particularly important in this regard. With 2,4,6-trimethylphenyl picryl ether

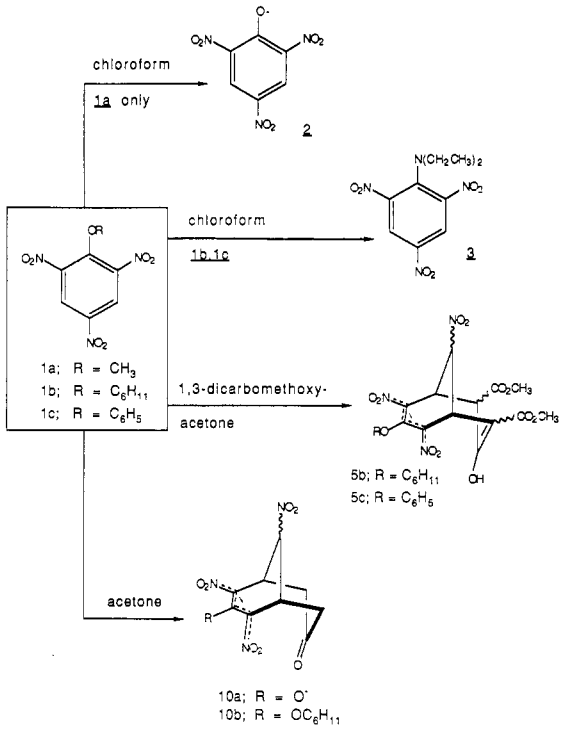
Scheme I. Reactions of Picryl Ethers with NEt_3



(1) Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667.
(2) Bernasconi, C. F. *J. Am. Chem. Soc.* **1971**, *93*, 6975.
(3) Crampton, M. R. *Adv. Phys. Org. Chem.* **1969**, *7*, 211.
(4) Fendler, J. H.; Fendler, E. J.; Griffen, C. E. *J. Org. Chem.* **1969**, *34*, 689.
(5) Servis, K. L. *J. Am. Chem. Soc.* **1967**, *89*, 1508.
(6) Clapp, L. B.; Lacey, H.; Beckwith, G. G.; Srivastava, R. M.; Muhammed, N. *J. Org. Chem.* **1968**, *33*, 4262.

0022-3263/89/1954-0756$01.50/0

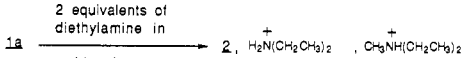
Scheme II. Reactions of Picryl Ethers with $HNEt_2$



$[(O_2N)_3C_6H_2OC_6H_2(CH_3)_3]$ attack by amine occurs on the picryl ring carbon bearing the trimethylphenoxy function.[6] This yields an observable σ complex intermediate, which decomposes to 2,4,6-trimethylphenoxide anion and picramide, a typical S_NAr substitution process. In contrast, TNA reacts with amines by *both* S_NAr and S_N2 mechanisms.[5-7] In methanol picramides are formed, whereas in toluene demethylation occurs to give picrate, **2**.[6]

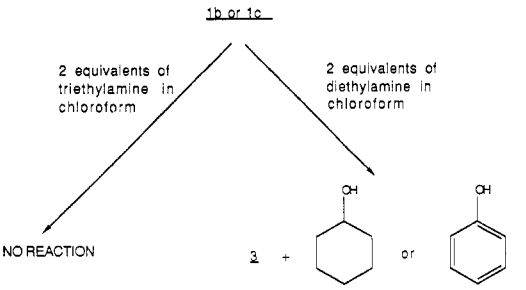
Results and Discussion

We have found that in chloroform, diethylamine (2 equiv) demethylates **1a** to yield **2**. NMR analysis shows the initially formed diethylmethylammonium cation resulting from demethylation equilibrates with diethylamine, resulting in the formation of methyldiethylamine. This latter amine then demethylates additional TNA. The result is a solution of picrate anion with several cations, from which diethylmethylammonium picrate crystallizes.

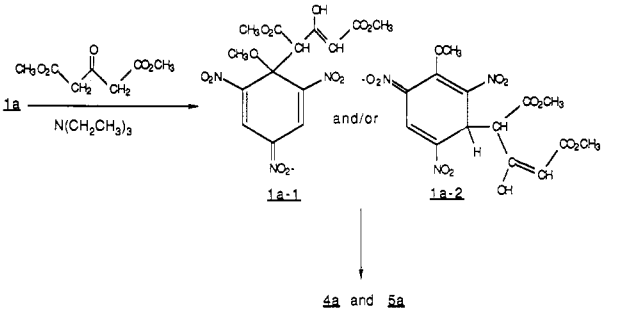


The more hindered cyclohexyl and phenyl picryl ethers **1b** and **1c** react with 2 equiv of diethylamine in chloroform to yield *N,N*-diethylpicramide, **3**, confirming similar observations made by Clapp[6] who isolated *N-tert*-butylpicramide from the reaction of *tert*-butylamine with both phenyl- and 2,4,6-trimethylphenyl picryl ethers. Interestingly, **1b** and **1c** do not react at all with triethylamine in chloroform, whereas **1a** is rapidly demethylated in this solvent.

In an acidic solvent like 1,3-dicarbomethoxyacetone, the reactions which occur are dramatically different. Enolate is rapidly formed when triethylamine is added to this more acidic carbon acid. Enolate addition to **1a** yields intermediate σ complexes **1a-1** and **1a-2**, which undergo further intramolecular cycloaddition to give the bridged ions **4a** and **5a**. Such meta-bridged products have previously been



reported to form with aromatic substrates under similar conditions.[8] The crude mixture of **4a** and **5a** was recrystallized to give well-formed crystals of *each compound*. Crystals of **4a** are orange whereas those of **5a** are bright yellow. Because of this color difference the compounds were easily separated by hand (picking crystals of each color from the mixture) and characterized by proton NMR spectroscopy. The color difference results from ether-oxygen substitution on the nitropropenenitronate functionality. Unsubstituted nitropropenenitronates absorb at ca. 500 nm.[9] Replacing one of the nitro groups with a cyano or carbomethoxy group,[9] or substituting functionality on the central carbon atom (as in the present study), results in a shift to shorter wavelength.



Compound **4a** is the first bicyclic nitropropenenitronate prepared with bridgehead functionality. All 1-substituted 2,4,6-trinitroaromatic substrates bridged previously yielded only products analogous to **5a**.[8] The detailed structural features of the bicyclic compounds obtained in the present study were elucidated by proton NMR.

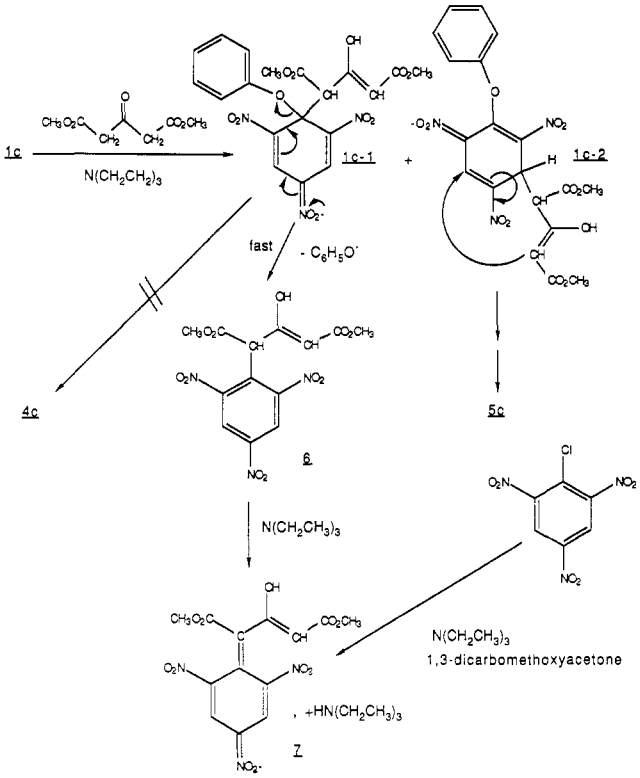
With the more hindered cyclohexyl and phenyl aromatic ether substrates **1b** and **1c**, reactions with 1,3-dicarbomethoxyacetone and triethylamine are quite different. With the phenoxy picryl ether **1c** both C-1 and C-3 addition complexes **1c-1** and **1c-2** are apparently formed. Complex **1c-1** cannot be observed and is not long-lived enough for intramolecular cyclization to the bridgehead-substituted bicyclic anion **4c** to occur. This is because phenoxide is a particularly good leaving group. It rapidly departs, allowing completion of S_NAr substitution and concomitant formation of 1-picryl-1,3-dicarbomethoxyacetone, **6**. The α-hydrogen of this product is sufficiently acidic so that the salt **7** is obtained as a final product. This is the same product obtained from the reaction of picryl chloride, 1,3-dicarbomethoxyacetone, and triethylamine.

The isomeric complex **1c-2** in which enolate is bonded to an unsubstituted carbon cannot lead to an S_NAr substitution product. The result in this case is therefore intramolecular cyclization to **5c**, similar to the reactions that occur with **1a**. As noted above, however, with TNA *both* bridgehead- and nitronate-substituted bicyclic anions are

(7) Gitis, S. S.; Morazova, T. I.; Glaz, A. I.; Kaminskii, A. Ya.; Golopolosova, T. V. *Zh. Org. Khim.* **1976**, *12*, 1935.

(8) Strauss, M. J. *Acc. Chem. Res.* **1974**, *7*, 181.

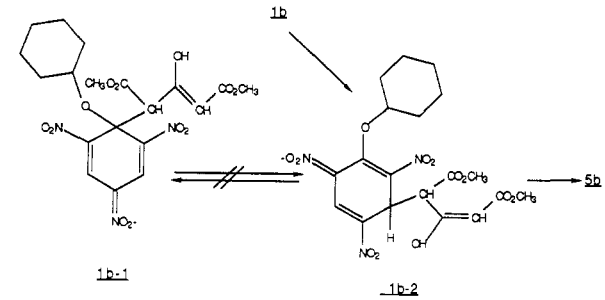
(9) Strauss, M. J.; Buncel, E.; Crampton, M. R.; Terrier, F. *Electron Deficient Aromatic- and Heteroaromatic-Base Interactions, The Chemistry of Anionic Sigma Complexes*, Elsevier: Amsterdam, 1984.



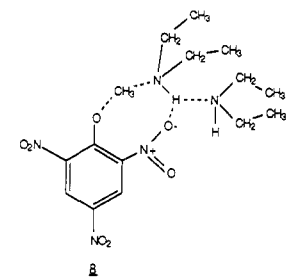
formed because methoxide is a much poorer leaving group than phenoxide.

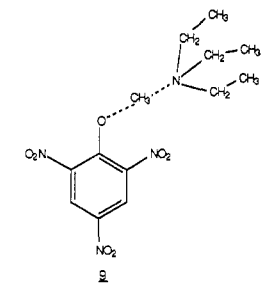
As noted above, the likely intermediates in the bridging reactions of **1a** are the C-1 and C-3 complexes **1a-1** and **1a-2**. In the case of the phenoxypicryl ether **1c**, the resultant complex **1c-2** leads only to the bridged ion **5c** in which the phenoxy function is on the central carbon of the nitropropenenitronate function. Though it might appear that **1c-2** could yield **4c** as well (with bridgehead substitution), the observation that it does not is evidence supporting **1a-1** as the direct precursor to **4a** and **1a-2** as the direct precursor to **5a**. Speculation about this regiospecificity in meta-bridging reactions has previously been made,[8,9] and the additional observations made in this study provide more evidence for the pathways by which these bicyclic structures are formed.

When *both* S_NAr and S_N2 displacement are unlikely, as in the cyclohexyl picryl ether **1b**, only the bridged ion **5b** is obtained. This must come from the C-3 precursor complex **1b-2**. The C-1 complex **1b-1** is therefore not on the reaction coordinate leading to product. The reason for this is apparent upon examining Dreiding models, which show substantial steric compression around the tetrahedral carbon of the trinitrocyclohexadienate ring in **1b-1**.



Again, interesting differences in reactivity are observed when the reactions of picryl ethers **1a–c** with dicarbomethoxyacetone are carried out in the presence of diethylamine instead of triethylamine. With **1a**, instead of bridged products like **4a** and **5a**, only demethylation to methyldiethylammonium picrate occurs. This is likely a result of stability conferred on the transition state for demethylation by hydrogen bonding as shown in **8**. Such stabilization cannot occur with **9** (reaction with triethylamine). While triethylamine can demethylate **1a** in chloroform, bridging of this substrate with 1,3-dicarbomethoxyacetone in the presence of triethylamine indicates that addition to the ring by enolate is a more favorable reaction pathway. This is not so in the presence of diethylamine, perhaps due, in part, to the lower energy of **8**. Such hydrogen bonding has previously been observed by Bernasconi who obtained direct kinetic evidence for stabilization by hydrogen bonding as shown in **8**.[10] We have also reported ortho nitro group interactions, similar to that proposed here, to explain the unusual stability of σ complexes prepared from cyclic ketones and 1,3,5-trinitrobenzene.[11]





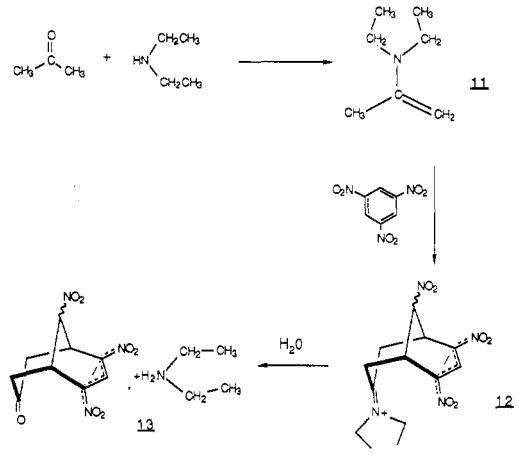
When dealkylation is blocked, as in **1b** and **1c**, the reactions with 1,3-dicarbomethoxyacetone and diethylamine yield the corresponding bridged ions **5b** and **5c**. In the reaction of **1c** trace amounts of the substitution product **7** can also be detected.

When the reactions of **1a–c** are carried out with di- and triethylamine in acetone, different products are again isolated. With triethylamine, **1a** is rapidly demethylated to give methyltriethylammonium picrate. This also occurs with diethylamine, but in this case reaction continues on to yield the meta-bridged ion **10a**, which is also readily formed from picric acid and diethylamine in acetone. When the reaction with **1a** is run at relatively low reactant concentration both demethylation product, picrate, as well as bridged product **10a**, can be detected. At higher concentrations, *only* **10a** is formed.

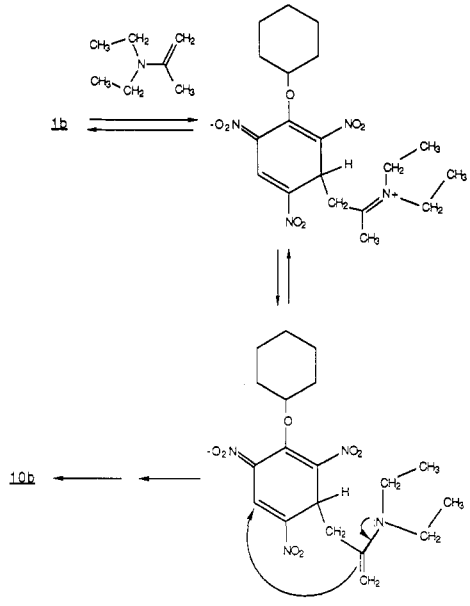
Meta-bridging reactions of 1,3,5-trinitrobenzene[12] and of picrate[13] with acetone have previously been reported by us,[12] as well as by Momose and co-workers.[13] Such reactions were proposed to occur through enamine intermediates, but this supposition was not supported by direct observation of such species. We have previously isolated enamine intermediates in the meta-bridging reactions of 3-pentanone.[14] These were obtained by adding the enamine prepared from this ketone and diethylamine to 1,3,5-trinitrobenzene.[14] However, prior attempts to prepare the extremely reactive enamine of acetone and diethylamine failed, and confirmation of a mechanistic scheme for this system was not possible. We have finally been able to prepare this very reactive species, **11**, from 2-(*N*,*N*-diethylamino)-2-propanenitrile, using a method described by Albrecht.[15] It was distilled directly from the reaction

(10) Bernasconi, C. F. *J. Phys. Chem.* **1971**, *75*, 3636.
(11) Renfrow, R. A.; Strauss, M. J.; Terrier, F. *J. Org. Chem.* **1980**, *45*, 471.
(12) Strauss, M. J.; Schran, H. *J. Am. Chem. Soc.* **1969**, *91*, 3974.
(13) Kabeya, T.; Kohashi, K.; Ohkura, Y.; Momose, T. *Chem. Pharm. Bull.* **1973**, *21*, 2168.
(14) Schran, H.; Strauss, M. J. *J. Org. Chem.* **1971**, *36*, 856.

vessel into a solution of the appropriate electron-deficient aromatic under anhydrous conditions, and the intermediate bridged zwitterion **12** could then be isolated. This readily hydrolyzes to the ketonic bridged structure **13**.



A similar bridged product, **10b**, is obtained from the cyclohexyl ether **1b** when it is treated with diethylamine in acetone. No bridgehead-substituted bicyclic ion is detected in this reaction. This is again supportive of a mechanism involving intermediate σ complex precursors, formed from either enolate or enamine attack at the C-3 rather than C-1 position. C-3 attack is also observed when acetone in the presence of triethylamine adds to **1b** or **1c** to give the σ complexes **14b** and **14c**, which are in equilibrium with the starting aromatics.



Experimental Section

All melting points are uncorrected. NMR spectra were recorded on a Bruker (Wp-270SY) FT-NMR spectrometer, and chemical shifts (δ) are reported with respect to internal TMS. IR and visible spectra were recorded on Perkin-Elmer 1430 and Lambda 4B spectrophotometers, respectively. Mass spectra were recorded on a Finnigan 4610 quadrupole instrument at 70 eV. Elemental analyses were performed by G. I. Robertson Laboratory, Madison, NJ.

Acetone, methylene chloride, diethylamine, and triethylamine were dried and distilled from CaO, CaH_2, KOH, and K_2CO_3, respectively. Diethyl ether was distilled from sodium. 1,3-Dicarbomethoxyacetone (Aldrich) was used without further purification. Picryl chloride (Pfaltz & Bauer) and TNA (Eastman) were recrystallized from $CHCl_3$ and MeOH, respectively.

Yields of isolated products vary from around 50% for the bridged adducts to around 80% for picrates.

Preparation of 1b. Cyclohexanol (5 mmol) and picryl chloride (6 mmol) were dissolved in a minimum amount of dry methylene chloride. DABCO (5 mmol) was then added, and the dark red mixture was stirred overnight under N_2. The solution eventually turned yellow, and a solid separated. The reaction was then quenched with 10% HCl, the separated organic phase was washed with cold water and dried ($MgSO_4$), and the solvent was removed under vacuum. The resulting oil was dissolved in MeOH to give 0.535 g (35%) of crystalline **1b**: mp 98–99 °C;[16] ^{1}H NMR ($CDCl_3$) δ 8.81 (s, 2 H), 4.26 (m, 1 H), 2.05–1.15 (m, 10 H).

Preparation of 1c. Picryl chloride (10 mmol) was dissolved in 25 mL of dry methylene chloride. Sodium phenoxide (10 mmol) was then added, and the dark red solution was stirred vigorously until it turned light yellow and a precipitate of NaCl formed. This was filtered off, and the filtrate was cooled to −30 °C. The light yellow crystals that formed were filtered and dried under vacuum to give 1.13 g (37%) of **1c**: mp 154–156 °C;[17] ^{1}H NMR (DMSO-d_6) δ 9.25 (s, 2 H), 7.4–7.07 (m, 5 H).

Reaction of Picryl Ethers 1 with Diethylamine in Chloroform. The various picryl ethers **1a–c** (10 mg) were each dissolved in $CDCl_3$ (0.5 mL) in an NMR tube sealed with a rubber septum. Diethylamine (2 equiv) was injected, and the reaction was monitored by taking spectra at timed intervals.

Picryl ether **1a** yielded picrate, **2**, with a mixture of cations. The diethyldimethylammonium salt of **2** crystallized out in the NMR tube. It was filtered and dried under vacuum: mp 274–275 °C; ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 2 H), 3.59 (q, 4 H), 3.20 (s, 6 H), 1.46 (t, 6 H). Anal. Calcd for $C_{12}H_{18}N_4O_7$: C, 43.63; H, 5.50; N, 16.96. Found: C, 43.64; H, 5.23; N, 17.04.

Upon reaction with diethylamine, picryl ethers **1b** and **1c** yielded the picramide **3**: ^{1}H NMR ($CDCl_3$) δ 8.74 (s, 2 H), 3.18 (q, 4 H), 1.22 (t, 6 H). A pure sample of **3** was added to the NMR tube to confirm **3** as the sole product arising from the reaction of **1b** and **1c** with diethylamine.

Reaction of Picryl Ethers 1 with Triethylamine in Chloroform-*d*. The reactions of **1a–c** with triethylamine were carried out as described above for diethylamine. Trinitroanisole, **1a**, reacts with triethylamine to give **2** as its triethylmethylammonium salt:[5,18] mp 260 °C; ^{1}H NMR ($CDCl_3$) δ 8.87 (s, 2 H), 3.45 (q, 6 H), 3.09 (s, 3 H), 1.39 (t, 9 H). Anal. Calcd for $C_{13}H_{20}N_4O_7$: C, 45.34; H, 5.87; N, 16.27. Found: C, 45.23; H, 5.75; N, 16.21.

For **1b** and **1c** no reaction occurred after 2 days.

Reaction of Picryl Ethers 1 with 1,3-Dicarbomethoxyacetone and Triethylamine. The picryl ethers **1a–c** were each dissolved in a minimum amount of dry methylene chloride, and the solutions were kept under N_2. One equivalent of 1,3-dicarbomethoxyacetone was then added, followed by the addition of 2 equiv of triethylamine. After 24 h at room temperature, the solvent was removed under vacuum, and the oily residue was poured into 125 mL of anhydrous ether. The mixture was stirred vigorously for several hours until a fine powder separated out. This was filtered and dried under vacuum.

In the case of TNA, **1a**, the powder was recrystallized from a 1:4 mixture of Et_2O–MeOH to give a mixture of distinct orange and yellow crystals of **4a** (25%) and **5a** (75%), respectively, as their triethylammonium salts. These were separated by hand under a 3D binocular magnifier microscope. For **4a**: mp 148–150 °C; UV-vis (MeOH) λ_{max} 492 nm; ^{1}H NMR ($CDCl_3$) δ 8.8 (d, 1 H), 5.35 (d, 1 H), 5.0 (dd, 1 H), 4.2 (s, 1 H), 3.8 (s, 3 H), 3.77 (s, 3 H), 3.3 (s, 3 H), 3.1 (q, 6 H), 1.33 (t, 9 H). For **5a**: mp 161–162 °C; UV-vis (MeOH) λ_{max} 460 nm; ^{1}H NMR ($CDCl_3$) δ 5.38 (dd, 1 H), 5.2 (dd, 1 H), 4.35 (m, 1 H), 4.19 (d, 1 H), 3.82 (s, 6 H), 3.73 (s, 3 H), 3.1 (q, 6 H), 1.33 (t, 9 H). Anal. Calcd for $C_{20}H_{30}N_4O_{12}$ (mixture): C, 46.33; H, 5.83; N, 10.81. Found: C, 46.51; H, 5.61; N, 10.45.

Reaction of cyclohexyl picrate, **1b**, with 1,3-dicarbomethoxyacetone and triethylamine gave only **5b** as its triethylammonium salt: mp 103–105 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.34 (dd, 1 H), 5.17

(15) Albrecht, H.; Raab, W. *Synthesis* **1980**, 320.

(16) Sinnott, M. L.; Whiting, M. C. *J. Chem. Soc. B* **1971**, 965.
(17) Jackson, C. L.; Earle, R. B. *Am. Chem. J.* **1903**, *29*, 212.
(18) Strauss, M. J.; Johanson, R. G. *Chem. Ind.* **1969**, 242.

(dd, 1 H), 4.36 (dd, 1 H), 4.26 (d, 1 H), 4.08 (m, 1 H), 3.82 (s, 3 H), 3.75 (s, 3 H), 3.1 (q, 6 H), 2.1–1.1 (m, 10 H), 1.29 (t, 9 H).

Reaction of phenyl picrate, **1c**, with 1,3-dicarbomethoxyacetone and triethylamine yielded **5c** and **7** (as their triethylammonium salts) in a 1:2 ratio. For **5c**: ^{1}H NMR ($CDCl_3$) 7.25–6.8 (m, 5 H), 5.5 (dd, 1 H), 5.3 (dd, 1 H), 4.54 (dd, 1 H), 4.11 (d, 1 H), 3.82 (s, 3 H), 3.78 (s, 3 H), 3.0 (br q, 6 H), 1.23 (br t, 9 H). For **7**: ^{1}H NMR ($CDCl_3$) δ 8.65 (s, 2 H), 3.96 (m, 1 H), 3.7 (s, 3 H), 3.5 (s, 3 H), 3.02 (q, 6 H), 1.3 (t, 9 H). The absorptions for **7** were confirmed by addition of a sample of **7** prepared by an independent method (see experimental).

Reaction of Picryl Ethers with 1,3-Dicarbomethoxyacetone and Diethylamine. The reaction of **1a** with 1 equiv of 1,3-dicarbomethoxyacetone and 2 equiv of diethylamine was carried out in a fashion similar to that with triethylamine. In this reaction, however, **2** (as its diethylmethylammonium salt) is isolated as the only product: mp 177–178 °C; ^{1}H NMR ($CDCl_3$) δ 8.9 (s, 2 H), 5.5 (br s, 1 H), 3.88 (s, 3 H), 2.92 (q, 4 H), 1.18 (t, 6 H). Anal. Calcd for $C_{11}H_{16}N_4O_7$: C, 41.77; H, 5.11; N, 17.72. Found: C, 41.82; H, 5.02; N, 17.58.

With the cyclohexyl picryl ether **1b**, the product isolated was **5b** (as its diethylammonium salt): mp 73–75 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.52 (br s, 1 H, NH), 5.32 (dd, 1 H), 5.18 (dd, 1 H), 4.36 (dd, 1 H), 4.23 (d, 1 H), 4.05 (m, 1 H), 3.82 (s, 3 H), 3.75 (s, 3 H), 3.68 (q, 4 H), 2.1–1.3 (m, 10 H), 1.3 (t, 6 H).

The phenyl picryl ether **1c** gave **5c** (diethylammonium salt) as a fine brown powder: mp 59–60 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.2–6.7 (m, 5 H), 5.39 (dd, 1 H), 5.2 (dd, 1 H), 4.45 (dd, 1 H), 3.92 (d, 1 H), 3.77 (s, 3 H), 3.69 (s, 3 H), 2.75 (q, 4 H), 1.06 (t, 6 H).

Reaction of Picryl Ethers 1 with Acetone and Diethylamine. Various picryl ethers **1a–c** were each dissolved in the minimum amount of dry acetone. Diethylamine (2 equiv) was then added, and the dark reaction mixture was stirred at room temperature for 48 h. The solvent was then removed under vacuum to give a dark oil, which was poured into 125 mL of anhydrous ether and stirred vigorously. After 24 h a fine powder precipitated from the mixture. This powder was filtered and dried under vacuum. In the reaction of **1a**, the powder was recrystallized from $CHCl_3$ to give yellow crystals of **10a**: mp 118–120 °C; ^{1}H NMR ($CDCl_3$) δ 5.05 (t, 1 H), 4.6 (M, 1 H), 3.08 (q, 4 H), 3.07 (s, 3 H), 2.92 (dd, 2 H), 2.72 (dd, 2 H), 1.3 (t, 6 H). Anal. Calcd for $C_{14}H_{22}N_4O_8$: C, 44.91; H, 5.92; N, 14.97. Found: C, 44.76; H, 5.63; N, 14.78.

Reaction of the cyclohexyl picryl ether, **1b**, yielded **10b** (as its diethylammonium salt): mp 135 °C dec; ^{1}H NMR (acetone-d_6) 5.55 (t, 1 H), 4.6 (m, 1 H), 4.08 (m, 1 H), 3.15 (q, 4 H), 2.92 (dd, 2 H), 2.75 (dd, 2 H), 1.95–1.4 (m, 10 H), 1.35 (t, 6 H). Anal. Calcd for $C_{19}H_{30}N_4O_8$: C, 51.57; H, 6.83; N, 12.67. Found: C, 51.86; H, 6.76; N, 12.32.

Reaction of Picryl Ethers 1 with Acetone and Triethylamine. The procedure above was used with triethylamine instead of diethylamine. In this reaction **1a** yielded the demethylation product **2** (as its triethylmethylammonium salt). It precipitated out of the reaction mixture as a yellow powder and was filtered and dried under vacuum: mp 260 °C; ^{1}H NMR (DMSO-d_6) 8.62 (s, 2 H), 3.25 (q, 6 H), 2.9 (s, 3 H), 1.2 (t, 9 H). Anal. Calcd for $C_{13}H_{20}N_4O_7$: C, 45.34; H, 5.85; N, 16.28. Found: C, 45.60; H, 5.62; N, 16.18.

When this reaction was carried out with **1b**, no precipitate formed after ethereal workup. Upon stirring in ether the originally dark red-purple solution turned yellow. An NMR experiment was then carried out in order to determine what was occurring. Picryl ether **1b** (20 mg) was dissolved in 0.5 mL of acetone-d_6 in an NMR tube sealed with a rubber septum. Triethylamine (18 μL, 2 equiv) was then added, and the reaction was monitored by ^{1}H NMR. Changes in the spectrum of the starting materials occurred very slowly. After 3 days the absorptions were consistent with a mixture of 75% of the starting ether **1b** and 25% of **14b**: ^{1}H NMR δ 8.42 (d, 1 H), 5.22 (d, 1 H), 4.10 (m, 1 H), 2.0–1.1 (m, 10 H); UV–vis (acetone) λ_{max} 439, 519 nm.

Preparation of 7 from Picryl Chloride. Picryl chloride (0.5 g) was dissolved in 5 mL of dry methylene chloride. 1,3-Dicarbomethoxyacetone (0.3 mL, 1 equiv) was added, followed by triethylamine (0.56 mL, 2 equiv). The dark red-purple reaction mixture was stirred at room temperature for 12 h. The methylene chloride was removed at reduced pressure, and the oily residue was washed with copious amounts of anhydrous ether (3 × 125 mL) to yield a dark purple powder: mp 98–100 °C dec; UV–vis λ_{max} 474 nm; ^{1}H NMR ($CDCl_3$) δ 8.68 (s, 2 H), 3.98 (br s, 1 H), 3.7 (s, 3 H), 3.5 (s, 3 H), 3.05 (q, 6 H), 1.32 (t, 9 H).

Preparation of 12. TNB (0.5 g, 2.35 mmol) was dissolved in a minimum amount of dry CH_2Cl_2 in a 25-mL round-bottom flask. Enamine **11**, made by the method of Albrecht,[15] was distilled directly into it. The temperature was kept at −78 °C during the addition by cooling the flask in a dry ice–acetone bath. Approximately 1 g of enamine was added (as determined by weight difference), and the mixture was allowed to warm up to room temperature for 12 h (under N_2). The red powder that precipitated from the solution was filtered under N_2 and dried under vacuum to give zwitterion **12**: mp 136–138 °C dec; ^{1}H NMR (acetone-d_6) δ 8.45 (s, 1 H), 5.65 (t, 1 H), 4.6 (m, 2 H), 4.2–3.9 (m, 4 H), 2.85 (br q, 4 H), 1.3 (t, 6 H); IR (KBr) ν_{max} 3000–2900, 2375, 1551, 1480, 1410, 1375, 1350, 1260, 1175, 1100, 1031, 880, 785, 749, 615 cm^{-1}; MS m/e (relative intensity) 214.1 (10.6), 213.1 (100), 167.06 (9.63), 120.1 (17.41), 113.23 (16.35), 91.12 (10.5), 84.2 (15.3), 75.16 (65.4), 74.15 (42.06), 73.20 (13.5), 70.19 (12.6), 63.14 (10.37), 58.20 (29.9). Anal. Calcd for $C_{13}H_{18}N_4O_6$: C, 47.84; H, 5.57; N, 17.17. Found: C, 47.66; H, 5.62; N, 16.96.

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