g, 3.0 mmol) was added 25 mL of a water solution of silver *p*-toluenesulfonate (0.87 g, 3.0 mmol), and the mixture was heated to 100 °C for 30 min. After cooling, the precipitate (AgI) was filterd off, the filtrate was condensed, and the residue was recrystallized from ethanol to give the product in 74% yield, mp 250 °C.

IR (solid/KBr) ν (cm^{-1}): 2220, 2190 (C≡C). Anal. Calcd for $C_{21}H_{18}NO_3SCl$: C, 63.07; H, 4.54; N, 3.50. Found: C, 62.96; H, 4.45; N, 3.54.

(4-Chlorophenyl)(4-methylpyridiniumyl)acetylene Methyl Sulfate (7, X = Cl). 25 mL of a dimethyl sulfate solution of (4-chlorophenyl)(4-pyridyl)acetylene (4.0 g, 18.8 mmol) was heated to 100 °C to complete solution. After cooling, the precipitate was filtered and recrystallized from methanol to give the methyl sulfate in 69% yield, mp 212 °C.

IR (solid/KBr) ν (cm^{-1}): 2230, 2200 (C≡C), 1260 (SO). ^1H NMR (270 MHz, DMSO-d_6) δ 9.001 (d, 2 H, pyridyl-3′,5′), 8.257 (d, 1 H, pyridyl-2′,6′), 7.756 (d, 2 H, phenyl-3,5), 7.630 (d, 2 H, phenyl-2,6), 4.328 (s, 3 H, NCH_3), 3.382 (s, 3 H, $CH_3SO_4^-$). Anal. Calcd for $C_{15}H_{14}NO_4SCl$: C, 53.02; H, 4.15; N, 4.12. Found: C, 52.46; H, 4.08; N, 4.10.

(4-Chlorophenyl)(4-methylpyridiniumyl)acetylene Picrate (8, X = Cl). 15 mL of a water solution of (4-chlorophenyl)(4-methylpyridiniumyl)acetylene methyl sulfate (0.69 g, 2.03 mmol) was warmed to complete solution. To the solution was added 10 mL of a water solution of picric acid (0.50 g, 2.2 mmol), and it was cooled. The precipitate was filtered and recrystallized from water–ethanol (3:1) to give the picrate in 76% yield, mp 212 °C.

IR (solid/KBr) ν(cm^{-1}): 2220, 2190 (C≡C). Anal. Calcd for $C_{20}H_{13}N_4O_7Cl$: C, 52.58; H, 2.87; N, 12.27; Cl, 7.76. Found: C, 51.97; H, 2.75; N, 12.01; Cl, 7.54.

(4-Chlorophenyl)(4-methylpyridiniumyl)acetylene Chloride (9, X = Cl). 25 mL of a water solution of (4-chlorophnyl)(4-methylpyridiniumyl)acetylene picrate (0.5 g, 1.1 mmol) was warmed to complete solution. To the solution was added 1 N hydrochloric acid (10 mL), and it was extracted with toluene and ether to remove picric acid. After the aqueous layer was condensed, the residue was recrystallized from methanol to give the chloride in 52% yield, mp 186 °C.

IR (solid/KBr) ν (cm^{-1}) 2210 (C≡C). Anal. Calcd for $C_{14}H_{11}NCl_2$: C, 63.65; H, 4.20; N, 5.30; Cl, 26.84. Found: C, 63.82; H, 4.11; N, 5.09; Cl, 26.53.

SHG Measurement. The compounds were ground in a mortar, meshed to 75–100 μm, and fixed on a glass slide by tape. The slide was irradiatd by a Nd:YAG laser (wavelength 1064 nm, pulse width 350 ps, power density 5 GW/cm^2, spot size 0.8 mm), and the intensity of SHG light (532 nm) was monitored by a photo diode and compared with the SHG intensity of urea.

Synthesis and Structure of 4,10-Diaza-5′-nitro-2,3-dibenzo-12-crown-4

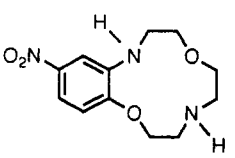
Richard A. Bartsch,*,† Thomas W. Robison,† Dhimant H. Desai,† Jan Krzykawski,† N. Kent Dalley,‡ and Weiming Jiang‡

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409, and Chemistry Department, Brigham Young University, Provo, Utah 84602

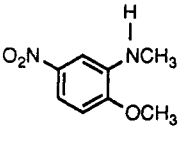
Received September 13, 1991

Introduction

Small-ring, mixed oxygen and nitrogen donor macrocycles interact strongly with a variety of heavy metal cations.[1] As part of a general program of mixed-donor macrocycle synthesis, we have prepared 4,10-diaza-5′-nitro-2,3-benzo-12-crown-4 (**1**). This ligand possesses a benzo-12-crown-4 ring system in which two oxygen donor atoms are replaced by nitrogens. For ligands derived from **1**, reduction of the nitro group would provide a potential attachment site for a chromogenic group[2] or modification for coupling with a monoclonal antibody.[3]



1



2

The ^1H NMR spectrum of **1** was unusual in that the chemical shift for the alkylarylamine hydrogen was further downfield than anticipated. To probe the reason for this anomaly, acyclic model compound **2** was synthesized and the crystal structure of **1** was determined. The synthetic routes to **1** and **2**, their ^1H NMR spectra, and the solid-state structure of **1** are now reported.

Results and Discussion

Synthesis. The preparation of macrocycle **1** in four steps from commercially available 2-amino-4-nitrophenol is shown in Scheme I. Reaction of 2-amino-4-nitrophenol with $TsOCH_2CH_2NHTs$[4] and K_2CO_3 in DMF gave tosyl amide **3** in 36% yield. Substitution of *N*-tosylaziridine[5] as the alkylating agent gave the same yield of **3**. For conversion of **3** into ditosyl amide **4**, reaction with tosyl chloride and pyridine in dichloromethane gave a good yield (69%) and easier workup than when pyridine was utilized as both the base and solvent. Cyclization of ditosyl amide **4** with the dimesylate of diethylene glycol and K_2CO_3 in DMF was achieved in 67% yield. This cyclization yield is appreciably higher than that obtained when the ditosylate of diethylene glycol was utilized. Deprotection of **4** by heating in concentrated H_2SO_4 at 100 °C gave a higher yield (60%) of mixed-donor macrocycle **1** than did the alternative deprotection method of heating with 30% HBr in acetic acid and phenol at reflux[6] (50% yield).

Although **2** is a known compound, it was previously isolated in low yield as a minor product from the exhaustive methylation of 2-amino-4-nitrophenol.[7] Reaction of 2-amino-4-nitrophenol with tosyl chloride and pyridine in dichloromethane gave a 77% yield of 4-nitro-2-(*p*-toluenesulfonamido)phenol (**6**) which was subsequently dimethylated with iodomethane and K_2CO_3 in DMF to provide *N*-methyl-4-nitro-2-(*p*-toluenesulfonamido)anisole (**7**) in 91% yield. Deprotection of **7** by heating in concentrated sulfuric acid at 100 °C produced a 91% yield of model compound **2**.

The structures of all new compounds were verified by IR, ^1H NMR spectra, and elemental analysis.

^1H NMR Spectra. Absorptions for the amine hydrogens in macrocycle **1** in deuteriochloroform appeared as broadened singlets at δ 1.86 and 6.15.[8] Ordinarily the chemical shift for a dialkylamine hydrogen occurs in the range of δ 0.5–3.0 and for an aromatic amine hydrogen at

† Texas Tech University.
‡ Brigham Young University.

(1) Lindoy, L. F. *Cation Binding by Macrocycles*; Inoue, Y.; Gokel, G. W.; Eds.; Marcel-Dekker: New York, 1990, p 599–629.
(2) Takagi, M.; Nakamura, H.; Ueno, K. *Anal. Lett.* **1977**, *10*, 1115.
(3) Moi, M. K.; Yanuck, M.; Deshpande, S. V.; Hope, H.; Denardo, S. J.; Meares, C. F. *Inorg. Chem.* **1987**, *26*, 3458.
(4) Hope, D. B.; Horncastle, K. *J. Chem. Soc. C* **1966**, 1090.
(5) Martin, A. E.; Ford, M. T.; Bulkowshi, J. E. *J. Org. Chem.* **1982**, *47*, 412.
(6) Haskell, E.; Bowlus, S. P. *J. Org. Chem.* **1976**, *41*, 159.
(7) Ingold, C. K.; Ingold, E. H. *J. Chem. Soc.* **1926**, 1310.
(8) The chemical shift values were not concentration dependent.

0022-3263/92/1957-1625$03.00/0

Scheme I

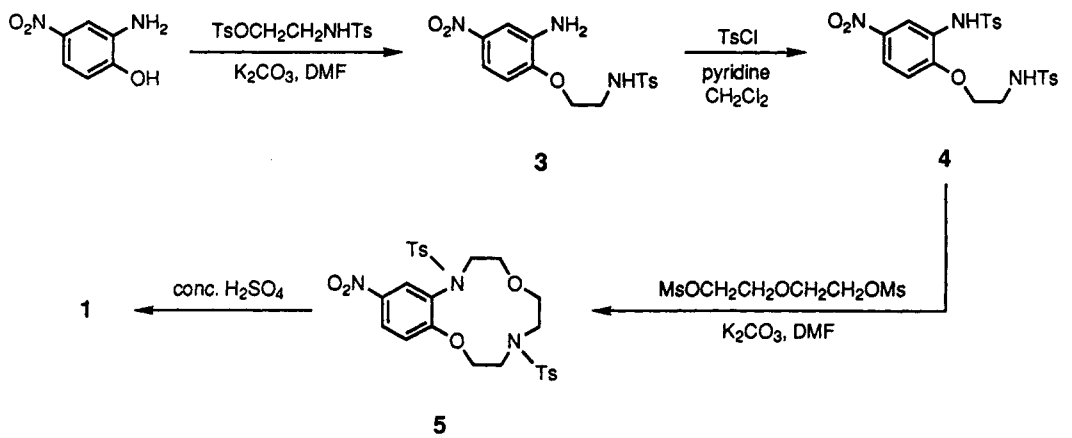


Table I. Data for Potential Hydrogen Bonds in 1

D–H···A	bond distances, Å D···A	H···A	bond angles, deg D–H···A	symmetry translation of A
N10 HN10 01	2.718 (5)	2.43[a]	96[a]	x, y, z
N10 HN10 N4	3.103 (5)	2.34	137	x, y, z
N10 HN10 07	2.818 (3)	2.39	107	x, y, z
N4 HN4 07	3.207 (5)	2.40	180	$-x, 1-y, 1-z$

[a] Since hydrogen atom positions were not refined, no esd values involving these atoms can be calculated.

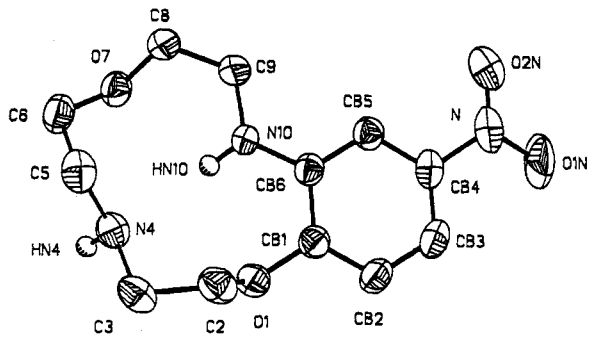


Figure 1. Molecular numbering scheme and crystal structure for 1.

δ 3.0–5.0.[9] Thus the chemical shift for the alkylarylamine hydrogen in 1 is appreciably outside of the anticipated range. For the acyclic model compound 2, the chemical shift of the broadened singlet for the alkylarylamine hydrogen was observed at δ 4.40[8] which demonstrates that proximity of the alkyl aryl ether oxygen in 1 is not responsible for the unusual chemical shift of the NH absorption.

Crystal Structure of Macrocycle 1. An X-ray structural study of 1 was undertaken to probe the environments of the two amine hydrogens. The computer drawing and numbering scheme for 1 are given in Figure 1. The figure clearly shows that dialkylamine hydrogen HN4 points away from the macrocyclic cavity while the alkylarylamine hydrogen HN10 points into the cavity and is approximately equidistant from O1, N4, and O7. These interatomic distances are shown in Table I. The data in Table I suggest an intramolecular hydrogen bond involving N10–HN10···N4 with an angle about HN10 of 137°. There may also be weak hydrogen bonding with O1 and O7, but the angles about HN10 involving those interactions are closer to 90° and 180°. There is an intermolecular hydrogen bond between the dialkylamine hydrogen HN4 and O7 of a symmetry related molecule (see Table I). The dihedral angle between the plane of the benzene ring and the least squares plane of the four heteroatoms of the heterocyclic ring is 173.4°. Deviations of the heteroatoms from this plane are as follows: O1, –0.19 Å; N4, 0.17 Å; O7, –0.18 Å; and N10, 0.20 Å. Deviations of the amine hydrogens from this plane are as follows: HN4, –0.62 Å; HN10, –0.29 Å. The dihedral angle between the plane of the nitro group (CB4, N, O1N and O2N) and the plane of the benzene ring is 7.9°.

In light of the intramolecular hydrogen bonding of the alkylarylamine hydrogen of 1 with the transannular dialkylamine nitrogen atom in the solid state, it seems virtually certain that such intramolecular hydrogen bonding also occurs in solution and is responsible for the downfield shift of the alkylarylamine hydrogen in the ^{1}H NMR spectrum. Positioning of the alkylarylamine hydrogen within the macrocyclic cavity places it within the deshielding region for the ring current of the benzene ring which will also cause a downfield shift from the usual position.

Experimental Section

^{1}H NMR spectra were taken at 200 MHz in $CDCl_3$.

Materials. Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. DMF was dried overnight over K_2CO_3, filtered, and distilled from CaH_2 under reduced pressure.

2-Amino-4-nitro-1-[2′-(*p*-toluenesulfonamido)ethoxy]-benzene (3). Anhydrous K_2CO_3 (13.90 g, 99.9 mmol), 2-amino-4-nitrophenol (7.00 g, 45.4 mmol), and DMF (30 mL) were heated and stirred at 100 °C for 0.5 h, and a solution of $TsOCH_2CH_2NHTs$[4] (16.78 g, 45.4 mmol) in DMF (30 mL) was added during a 10-h period with a syringe pump. The reaction mixture was stirred for an additional 2 h at this temperature, and the solvent was evaporated in vacuo. Water and EtOAc were added to the residue, and the organic layer was separated, dried ($MgSO_4$), and evaporated in vacuo to give an oil which was filtered through a short column of alumina with Et_2O as eluent. The solvent was evaporated in vacuo, and cold CH_2Cl_2 (100 mL) was added to the residue, precipitating a yellow solid which was filtered and washed with cold CH_2Cl_2 to give 5.75 g (36%) of 3 as a yellow powder: mp 181–182 °C; IR (KBr) 3414, 3333 (NH), 1521 (NO_2), 1342, 1150 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 3.34 (q, J = 4.5 Hz, 2 H), 3.97 (t, J = 5.0 Hz, 2 H), 5.00 (br s, 2 H), 6.59 (d, J = 8.2 Hz, 1 H), 7.23 (d, J = 8.2 Hz, 2 H), 7.45–7.60 (m, 2 H), 7.74 (d, J = 8.2 Hz, 2 H), 7.85 (br s, 1 H); ^{13}C NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 20.58, 41.34, 66.32, 107.36, 108.72, 112.32, 125.82, 128.78, 137.35, 141.18, 142.15, 149.81. Anal. Calcd for $C_{15}H_{17}N_3O_5S$: C, 51.27; H, 4.88. Found: C, 51.39; H, 4.93.

(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974; p 178.

4-Nitro-2-(*p*-toluenesulfonamido)-1-[2′-(*p*-toluenesulfonamido)ethoxy]benzene (4). Sulfonamide **3** (5.15 g, 14.7 mmol) was suspended in CH_2Cl_2 (250 mL) and pyridine (14 mL). *p*-Toluenesulfonyl chloride (4.19 g, 22.0 mmol) was added in one portion, and the mixture was stirred at rt for 2 h. The reaction mixture was washed with 5% HCl and then water. The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated in vacuo to give a yellow solid which was washed with cold CH_2Cl_2 to give **4** (5.14 g, 69%) as a white solid: mp 188.5–189.5 °C; IR (KBr) 3327, 3223 (NH), 1528 (NO_2), 1343, 1162 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 2.31 (s, 3 H), 2.36 (s, 3 H), 3.13 (q, J = 5.0 Hz, 2 H), 3.67 (t, J = 4.8 Hz, 2 H), 6.55 (d, J = 9.1 Hz, 1 H), 7.03 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.59 (d, J = 8.3 Hz, 2 H), 7.75 (d, J = 8.3 Hz, 2 H), 7.85–8.05 (m, 2 H), 8.41 (d, J = 2.7 Hz, 1 H), 9.50 (s, 1 H); ^{13}C NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 21.04, 41.39, 66.94, 109.99, 119.42, 121.40, 126.31, 126.66, 128.91, 129.26, 136.53, 137.81, 141.05, 142.80, 143.19, 154.38. Anal. Calcd for $C_{22}H_{23}N_3O_7S_2$: C, 52.27; H, 4.59. Found: C, 52.29; H, 4.52.

4,10-Bis(*p*-toluenesulfonamido)-5′-nitro-2,3-dibenzo-12-crown-4 (5). Disulfonamide **4** (3.15 g, 6.23 mmol) and the dimesylate of diethylene glycol (1.63 g, 6.23 mmol) were dissolved in DMF (30 mL), and the solution was added with a syringe pump to a stirred suspension of K_2CO_3 (4.31 g, 31.2 mmol) in DMF (20 mL) during a 7-h period. The reaction mixture was stirred for an additional 17 h at rt, and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel with CH_2Cl_2–Et_2O (30:1) as eluent to give **5** (2.40 g, 67%) as a tan solid: mp 92–93 °C; IR (KBr) 1518 (NO_2), 1343, 1162 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 2.43 (s, 3 H), 3.20–4.00 (m, 10 H), 4.25 (t, J = 4.2 Hz, 2 H), 6.71 (dd, J = 1.7, 7.9 Hz, 1 H), 6.80–7.00 (m, 2 H), 7.15–7.40 (m, 4 H), 7.61 (d, J = 8.2 Hz, 2 H), 7.69 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.47, 50.98, 52.50, 68.83, 70.14, 71.53, 112.63, 128.86, 125.96, 127.24, 127.71, 129.30, 129.61, 129.84, 134.77, 135.64, 140.63, 143.85, 144.00, 162.82. Anal. Calcd for $C_{26}H_{29}N_3O_8S_2$: C, 54.25; H, 5.08. Found: C, 54.20; H, 5.04.

4,10-Diaza-5′-nitro-2,3-dibenzo-12-crown-4 (1). Macrocycle **5** (2.87 g, 4.99 mmol) was dissolved in concentrated H_2SO_4 (10 mL) and heated at 100 °C for 12 h under N_2. The reaction mixture was cooled in an ice bath, and Et_2O (200 mL) was added dropwise; a light gray precipitate formed. The solid was filtered and dissolved in a minimum amount of water. Solid KOH was added to pH >10, and an orange precipitate formed which was filtered. The filtrate was extracted several times with CH_2Cl_2, and the orange solid and organic extracts were combined. The solution was dried (Na_2SO_4) and evaporated in vacuo. The residue was passed through a short bed of alumina with CH_2Cl_2–MeOH (49:1) as eluent to provide **1** (0.80 g, 60%) as a yellow solid: mp 138–139 °C; IR (KBr) 3346 (NH), 1518, 1338 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$)[8] δ 1.86 (br s, 1 H), 2.75 (t, J = 4.7 Hz, 2 H), 2.87 (t, J = 4.7 Hz, 2 H), 3.39 (t, J = 4.7 Hz, 2 H), 3.56 (t, J = 4.8 Hz, 2 H), 3.65 (t, J = 4.7 Hz, 2 H), 4.22 (t, J = 4.5 Hz, 2 H), 6.15 (br s, 1 H), 7.00 (d, J = 8.6 Hz, 1 H), 7.45–7.65 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 44.29, 47.24, 47.58, 67.89, 68.86, 71.49, 107.01, 113.03, 117.75, 141.84, 144.22, 151.54. Anal. Calcd for $C_{12}H_{17}N_3O_4$: C, 53.92; H, 6.41. Found: C, 53.74; H, 6.33.

4-Nitro-2-(*p*-toluenesulfonamido)phenol (6). A stirred solution of 2-amino-4-nitrophenol (2.00 g, 13.0 mmol) and pyridine (1.13 g, 143 mmol) in CH_2Cl_2 (20 mL) was cooled to −3 °C in an ice–salt bath, and *p*-toluenesulfonyl chloride (2.47 g, 12.98 mmol) was added in one portion. The reaction mixture was allowed to warm to rt during a 5-h period. The mixture was washed with 6 N HCl which produced a precipitate. The solid was filtered and washed with water and then CH_2Cl_2 to give **6** (3.09 g, 77%) as a light brown solid: mp 206.5–208 °C; IR (KBr) 3395 (OH), 1529 (NO_2) 1345, 1159 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$ + $CD_3S(O)CD_3$) δ 2.36 (s, 3 H), 6.86 (d, J = 9.0 Hz, 1 H), 7.23 (d, J = 5.9 Hz, 2 H), 7.71 (d, J = 6.5 Hz, 2 H), 7.78–7.84 (dd, J = 2.9, 8.7 Hz, 2 H), 8.28 (d, J = 2.8 Hz, 1 H), 10.66 (br s, 1 H); ^{13}C NMR (CD_3Cl_3 + $CD_3S(O)CD_3$) δ 21.21, 114.74, 116.15, 121.08, 124.96, 126.92, 129.40, 135.66, 140.07, 143.85, 153.59. Anal. Calcd for $C_{13}H_{12}N_2O_5S$: C, 50.65; H, 3.92. Found: C, 50.34; H, 3.89.

***N*-Methyl-4-nitro-2-(*p*-toluenesulfonamido)anisole (7).** A mixture of tosylamide **6** (3.18 g, 10.0 mmol) K_2CO_3 (5.68 g, 22.0 mmol), and iodomethane (5.68 g, 40.0 mmol) in DMF (30 mL) was vigorously stirred and heated at 80 °C for 16 h. The mixture was evaporated in vacuo, and 100 mL of CH_2Cl_2 and 100 mL of water were added to the residue. The organic layer was separated, washed with water (2 × 50 mL), and dried ($CaCl_2$). Evaporation of the solvent in vacuo gave **7** (3.15 g, 91%): mp 119–121 °C; IR (KBr) 1589 (NO_2), 1344, 1157 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H), 3.19 (s, 3 H), 3.60 (s, 3 H), 6.92 (d, J = 9.0 Hz, 1 H), 7.30 (d, J = 8.5 Hz, 2 H), 7.57 (d, J = 8.3 Hz, 2 H), 8.13–8.20 (m, 2 H). Anal. Calcd for $C_{15}H_{16}N_2O_5S$: C, 53.56; H, 4.80. Found: C, 53.35; H, 4.75.

***N*-Methyl-2-methoxy-5-nitroaniline (2).** A solution of **7** (0.80 g, 2.3 mmol) in 15 mL of concentrated H_2SO_4 was heated at 100 °C for 16 h under N_2. The mixture was cooled to 0 °C in an ice bath, and 30 mL of 30% aqueous NaOH was added. The mixture was filtered and washed with 5 mL of water. The combined filtrate and washing were extracted with CH_2Cl_2 (3 × 40 mL). The organic layer was dried (K_2CO_3) and evaporated in vacuo to give **2** (0.38 g, 91%) as an orange solid: mp 85–87 °C (lit.[7] mp 87 °C); IR (KBr) 3448 (NH); 1529, 1336 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$)[8] δ 2.85 (d, J = 5.2 Hz, 3 H), 3.87 (s, 3 H), 4.40 (br s, 1 H), 6.67 (d, J = 8.8 Hz, 1 H), 7.28 (s, 1 H), 7.55 (dd, J = 2.7, 8.7 Hz, 2 H).

Acknowledgment. Research conducted at TTU was supported by a contract from Technicon Instruments Incorporated of Tarrytown, New York.

Registry No. **1**, 138572-06-2; **2**, 19871-39-7; **3**, 138572-07-3; **4**, 138572-08-4; **5**, 138572-09-5; **6**, 91956-17-1; **7**, 19871-31-9; $TsO(CH_2)_2NHTs$, 6367-75-5; $MsOCH_2CH_2OCH_2CH_2OMs$, 34604-52-9; 2-amino-4-nitrophenol, 99-57-0.

Supplementary Material Available: A description of the crystal determination for **1** and tables (1S–3S) which contain a summary of crystal and experimental data, structure solution details, atom postional and thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

On the Mechanism of the Reaction between Ketones and Trifluoromethanesulfonic Anhydride. An Improved and Convenient Method for the Preparation of Pyrimidines and Condensed Pyrimidines

A. García Martínez,* A. Herrera Fernández, and F. Moreno Jiménez

Departamento de Química Orgánica, Facultad de Ciencias, Químicas, Universidad Complutense, E-28040 Madrid, Spain

A. García Fraile

Departamento de Química Orgánica, Facultad de Ciencias, UNED, E-28040 Madrid, Spain

L. R. Subramanian and M. Hanack*

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II, Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Federal Republic of Germany

Received July 9, 1991 (Revised Manuscript Received November 25, 1991)

Introduction

Carbonyl compounds react with trifluoromethanesulfonic (triflic) anhydride to give products of different structure and stereochemistry. Ketones afford vinyl trifluoromethanesulfonates (triflates), while *gem*-ditriflates have been isolated from aldehydes and nonenolizable ketones.[1] Triflates have been found to be valuable starting

(1) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 82.

0022-3263/92/1957-1627$03.00/0