solid: mp 69–70 °C; IR (CH_2Cl_2) 3580, 2952, 2898, 1589, 1446, 1379, 1353, 1228, 1180, 1113, 1032, 839 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.30 (s, 18 H), 2.40 (s, 3 H), 4.61 (s, 1 H), 6.78 (s, 1 H), 7.12 (s, 1 H); mass spectrum, m/e 252 ($M^{\cdot+}$). Anal. Calcd for $C_{13}H_{24}OSi_2$: C, 61.82; H, 9.59. Found: C, 61.76; H, 9.65.

1-Bromo-2-methoxy-4-(trimethylsilyl)benzene (11). To **6b** (0.252 g) in dry CH_2Cl_2 (10 mL) under argon at −30 °C was added *N*-bromosuccinimide (0.179 g) in one portion. The solution was stirred at −30 °C for 20 min an then warmed to room temperature. The solvent was evaporated under reduced pressure and the residue triturated with hexane (3 × 20 mL). The combined extracts were washed with brine (10 mL) and dried. The solvent was evaporated under reduced pressure and the residue chromatographed (silica gel, hexane) to give **11** (0.218 g, 82%) as a colorless oil: IR (film) 3004, 2954, 2845, 1570, 1481, 1461, 1371, 1247, 1185, 1106, 1044, 885, 837, 754 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.30 (s, 9 H), 3.75 (s, 3 H), 6.85 (s, 1 H), 7.05 (d, 1 H, J = 7.0 Hz), 7.30 (d, 1 H, J = 7.0 Hz); mass spectrum, m/e 260, 258 ($M^{\cdot+}$). Anal. Calcd for $C_{10}H_{15}BrOSi$: C, 46.31; H, 5.84. Found: C, 46.52; H, 5.95.

1,5-Dibromo-2-methoxy-4-(trimethylsilyl)benzene (12). To **6b** (0.126 g) in dry CH_2Cl_2 (5 mL) was added bromine (0.160 g) dropwise. The resulting solution was stirred for 1 h at room temperature and washed with saturated aqueous sodium thiosulfate (2 mL) and brine (2 mL). The solvent was evaporated under reduced pressure and the residue chromatographed (silica gel, hexane) to give **12** (0.141 g, 84%) as white crystals: mp 91–93 °C (from hexane); IR (KBr) 2960, 2910, 2840, 1560, 1455, 1330, 1245, 1050, 840, 755 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 0.40 (s, 9 H), 3.90 (s, 3 H), 6.93 (s, 1 H), 7.69 (s, 1 H); mass spectrum, m/e 335 ($M^+ - 1$). Anal. Calcd for $C_{10}H_{14}Br_2OSi$: C, 35.50; H, 4.18. Found: C, 35.80; H, 4.05.

4-Methoxy-2,5-bis(trimethylsilyl)acetophenone (13). To $AlCl_3$ (0.667 g) in CH_2Cl_2 (10 mL) under argon was added AcCl (0.39 g). When all the $AlCl_3$ had dissolved, the solution was cooled to −78 °C and a solution of **6b** (1.23 g) in dry CH_2Cl_2 (15 mL) was added rapidly. The resulting solution was stirred at −78 °C for 30 min, allowed to warm up to 0 °C, and poured into saturated aqueous $NaHCO_3$ (15 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL), the combined organic phase was dried, and the solvent was evaporated under reduced pressure. The residue was chromatographed (silica gel, Et_2O/hexane 1:4) to give **13** (0.98 g, 67%) as a white solid: mp 101–102 °C; IR (CH_2Cl_2) 2947, 2899, 1671, 1576, 1511, 1456, 1358, 1335, 1227, 1121, 1041 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 0.27 (s, 18 H), 2.59 (s, 3 H), 3.88 (s, 3 H), 7.18 (s, 1 H), 7.95 (s, 1 H); mass spectrum, m/e 279 (M^+ − Me). Anal. Calcd for $C_{15}H_{26}O_2Si_2$: C, 61.15; H, 8.90. Found: C, 61.10; H, 8.95.

Registry No. **6a**, 113353-56-3; **6b**, 18405-84-0; **6c**, 113353-60-9; **7a**, 113353-57-4; **7c**, 113353-61-0; **8a**, 113353-58-5; **8b**, 113353-59-6; **8c**, 113353-62-1; **9b**, 113378-71-5; **11**, 113353-63-2; **12**, 113353-64-3; **13**, 113353-65-4; PhOMe, 100-66-3; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; 4-methylanisole, 104-93-8; phenol, 108-95-2.

A New Strategy for the Synthesis of Polyazamacrocyclic Compounds: Use of a Removable Protecting and Rigid Group

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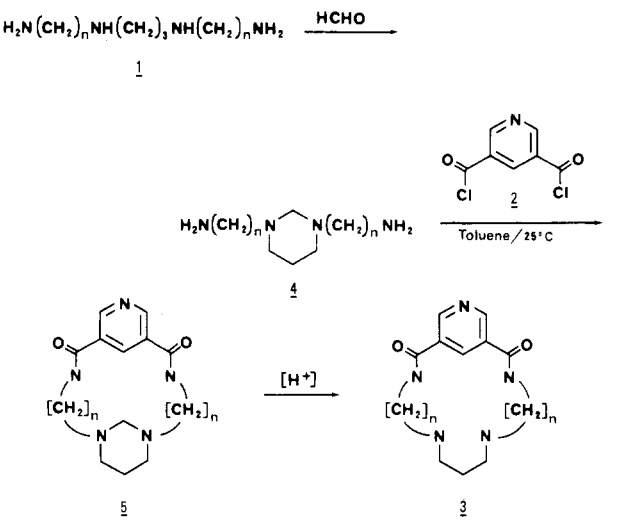
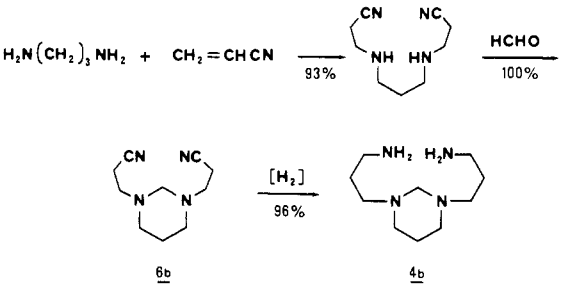
Within the past decade, the chemistry of macrocyclic ring systems has developed rapidly. Among the general strategies for ring closure reactions,[1] the high dilution principle[2] and the template effect[3] proved to be most profitable in that the formation of oligo- or polycondensation products is suppressed or minimized. The rigid group principle[4] has also been used to restrict the rotational possibilities by having a number of atoms composing the open-chain precursor held in the form of a rigid group.

Scheme I



Scheme II



The syntheses of pyridyl-containing polyazamacrocycles are mainly concerned with the template and high dilution methods. Our interest for compounds **3** incorporating a 3,5-disubstituted pyridino group prompted us to develop a convenient synthetic route for polyazamacrocycles incorporating available secondary amino groups. The general procedure for the preparation of polyazamacrocycles **3a–c** involves the reaction of the 3,5-pyridinedicarbonyl dichloride (**2**) with a twofold excess of the corresponding tetraamine **1a–c**. Although high dilution conditions were used, in all cases the overall yields were poor. We now report an efficient new procedure for the synthesis of macrocycles involving the temporary chemical modification of the linear precursor. This principle has been applied to linear tetraamines **1a–c** which are used in the preparation of polyazamacrocycles **3a–c**. The synthetic process is summarized in Scheme I.

Addition of an equimolar amount of formaldehyde (37% in water) to tetraamines **1a** and **1c** resulted in the formation of the six-membered aminals **4a** and **4c** (Scheme I). The reaction was very selective and only the six-membered rings were formed. Reaction of **1b** with formaldehyde always led to mixtures of variable amounts of differently substituted derivatives, probably due to the

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0022-3263/88/1953-1817$01.50/0

different possibilities of forming six-membered aminals. It was convenient in this case to prepare **4b** following the route depicted in Scheme II. Heating 1,3-diaminopropane with 2 equiv of acrylonitrile generated the *N,N'*-bis(2-cyanoethyl)-1,3-diaminopropane which was converted to the cyclic aminals **6b** by treatment with 37% formalin. Reduction of the nitrile groups with H_2-Raney nickel gave **4b** which was used as soon as it was generated. With time, **4b** underwent a slow transformation, giving rise to a mixture similar to that observed in the direct synthesis of **4b** from **1b** and formaldehyde.

Cyclization of aminals **4a–c** with 3,5-pyridinedicarbonyl dichloride afforded the corresponding macrocycles **5a–c** (Scheme I). Reactions were run under high dilution conditions. **5a–c** were obtained in fairly good yields (19%, 37%, and 26%, respectively). As expected, yields were lowered by increasing the concentration of the reagents; e.g., **5b** was prepared in 9% yield upon increasing the concentration fivefold. The treatment of **5a–c** with malonic acid in an ethanol–pyridine mixture led to the target molecules **3a–c**.

Compounds **3a–c** are new macroclyclic ligands[12] and their complexing properties are currently being investigated. In conclusion, macrocycles **3a** and **3c** were accessible in 10% and 17% overall yield from **1a** and **1c**, respectively, whereas the direct method yielded only minor amounts of **3a** and **3c** (0.2% and 1.8%, respectively). **3b** was obtained in 28% overall yield from 1,3-diaminopropane, compared to 1% from **1b**. These results demonstrate that the temporary chemical modification described here is a valuable new synthetic process in the preparation of macrocycles. The procedure is, in all probability, applicable to other macrocyclization reactions.

Experimental Section

Commercial chemicals were used without further purification, except for solvents, which were purified and dried before use by standard methods. Melting points are uncorrected. Yields are isolated yields. ^1H and ^{13}C NMR spectra were recorded with Bruker WP80SY and AM300 spectrometers and chemical shifts are reported in δ values (ppm) downfield from Me_4Si. ^1H NMR spectra of **5a–c** were recorded at 130–135 °C, as broad signals were observed at room temperature. Similarly the ^{13}C NMR spectrum of **5a** was recorded at 100 °C. In solution at room temperature these compounds slowly exchange between several conformers due to hindered rotation around the amide bonds. Mass spectra were run by the Service de Spectrometrie de Masse, USTMG-CNRS, Grenoble. Microanalyses were performed by the Service Central d'Analyses, CNRS. 3,5-Pyridinedicarbonyl dichloride[5] and tetraamines **1a–c**[6,7] were prepared according to the literature precedent. *N,N'*-Bis(2-cyanoethyl)-1,3-diaminopropane was prepared according to the method of Israel et al.[8]

Preparation of Cyclic Aminals. **4a** and **4c** were prepared from the corresponding tetraamines **1a** and **1c** through known procedures.[9]

1,3-Bis(2-aminoethyl)hexahydropyrimidine (4a). A solution of **1a** (8 g, 50 mmol) in 15 mL of water was cooled by means of an ice bath, formaldehyde (1 equiv, 37% in water) was added dropwise, and the reaction mixture was stirred for 1 h. The resulting reaction mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were dried (Na_2SO_4), and the solvent was removed in vacuo to afford a yellowish oil. Distillation under vacuum afforded **4a** as a colorless oil (76%, bp 95 °C (0.15 Torr)): ^1H NMR ($CDCl_3$) δ 3.16 (s, 2 H, NCH_2N), 2.3–2.9 (br m, 16 H, NCH_2 and NH_2), 1.5–1.9 (br m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 21.88 (CH_2), 37.42, 50.97, and 55.80 (NCH_2), 74.92 (NCH_2N). Anal. Calcd for $C_8H_{20}N_4$: C, 55.77; H, 11.70; N, 32.52. Found: C, 54.93; H, 11.92; N, 31.06.

1,3-Bis(4-aminobutyl)hexahydropyrimidine (4c). This compound was prepared as described for **4a** and was obtained as a colorless oil after distillation (90%, bp 155 °C (1 Torr)): ^1H NMR ($CDCl_3$) δ 3.08 (s, 2 H, NCH_2N), 2.16–2.82 (m, 12 H, NCH_2), 1.31–1.88 (m, 10 H, CH_2), 1.16 (s, 4 H, NH_2); ^{13}C NMR ($CDCl_3$) δ 23.44, 24.42, and 31.60 (CH_2), 41.89, 52.34, and 54.91 (NCH_2), 76.28 (NCH_2N). Anal. Calcd for $C_{12}H_{28}N_4$: C, 63.11; H, 12.36; N, 24.53. Found: C, 63.00; H, 12.36; N, 22.88.

1,3-Bis(2-cyanoethyl)hexahydropyrimidine (6b). The reaction was carried out in quantitative yield from *N,N'*-bis(2-cyanoethyl)-1,3-diaminopropane[8] as described for **4a**. **6b** decomposed above 120 °C and was used without purification: ^1H NMR ($CDCl_3$) δ 3.39 (s, 2 H, NCH_2N), 2.4–3.1 (m, 8 H, NCH_2), 1.5–1.9 (br m, 6 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 16.42 and 21.57 (CH_2), 49.16 and 51.38 (NCH_2), 73.84 (NCH_2N), 118.57 (C≡N). Anal. Calcd for $C_{10}H_{16}N_4 \cdot 2HCl$: C, 45.29; H, 6.84; N, 21.13. Found: C, 44.58; H, 7.40; N, 22.16 (mp 135–138 °C dec).

1,3-Bis(3-aminopropyl)hexahydropyrimidine (4b). This compound was obtained by reduction of the dinitrile derivative **6b** with H_2-Raney nickel according to the known procedure[10] (96%, bp 120 °C (1 Torr)): ^1H NMR ($CDCl_3$) δ 3.10 (s, 2 H, CH_2), 2.16–2.92 (m, 12 H, NCH_2), 1.43–1.88 (br m, 6 H, CH_2), 1.2 (s, 4 H, NH_2); ^{13}C NMR ($CDCl_3$) δ 22.89 and 30.33 (CH_2), 40.02, 51.95, and 52.39 (NCH_2), 75.93 (NCH_2N). Anal. Calcd for $C_{10}H_{24}N_4 \cdot H_2O$: C, 55.05; H, 11.93; N, 25.69. Found: C, 55.87; H, 11.00; N, 24.73.

General Procedure for Macrocycle Synthesis. All reactions were run under a nitrogen atmosphere. A solution of 3,5-pyridinedicarbonyl dichloride[5] (25 mmol) in toluene (200 mL) and a solution of the appropriate tetraamine **1** or **4** (12.5 mmol) in toluene (200 mL) were simultaneously slowly added to 1000 mL of toluene at room temperature under vigorous stirring. After addition, stirring was continued for 12–15 h. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to afford a white or yellowish solid which was purified by recrystallization from diethyl ether and acetone.

3,6,10,13,17-Pentaazabicyclo[13.3.1]nonadeca-1(19),15,17-triene-2,14-dione (3a) (0.2%; mp 262 °C): ^1H NMR ($CDCl_3$) δ 9.20 (d, 2 H, Ar H), 8.16 (br t, 1 H, Ar H), 7.68 (br, 2 H, NH), 3.27–3.70 (br m, 4 H, NCH_2), 2.63–3.08 (br m, 8 H, NCH_2), 1.51–2.00 (br m, 4 H, CH_2 and NH); ^{13}C NMR ($CDCl_3$) δ 31.10 (CH_2), 39.59, 48.25, and 46.65 (NCH_2), 129.74, 131.73, and 151.92 (Ar C), 164.73 (C=O); CI MS, *m/z* 292 (M + 1). Anal. Calcd for $C_{14}H_{21}N_5O_2$: C, 57.71; H, 7.26; N, 24.04. Found: C, 57.71; H, 7.27; N, 23.61.

3,7,11,15,19-Pentaazabicyclo[15.3.1]henicosa-1(21),17,19-triene-2,16-dione (3b) (1%, mp 208 °C dec): ^1H NMR ($CDCl_3$) δ 9.23 (d, 2 H, Ar H), 9.02 (br s, 2 H, NH), 7.95 (t, 1 H, Ar H), 3.49–3.80 (m, 4 H, NCH_2), 2.61–3.10 (m, 8 H, NCH_2), 1.5–1.98 (m, 8 H, CH_2 and NH); ^{13}C NMR ($CDCl_3$) δ 26.92 and 30.92 (CH_2), 41.28, 46.79, and 49.55 (NCH_2), 129.66, 129.86, and 152.13 (Ar C), 164.85 (C=O); EI MS, *m/z* 319 (M). Anal. Calcd for $C_{16}H_{25}N_5O_2$: C, 60.16; H, 7.89; N, 21.93. Found: C, 59.73; H, 7.88; N, 21.06.

3,8,12,17,21-Pentaazabicyclo[17.3.1]tricosa-1(23),19,21-triene-2,18-dione (3c) (1.8%, mp 232 °C dec): ^1H NMR ($CDCl_3$) δ 9.08 (d, 2 H, Ar H), 8.59 (br s, 2 H, NH), 8.35 (br t, 1 H, Ar H), 3.20–3.61 (br, 4 H, NCH_2), 1.16–2.88 (br m, 20 H, NCH_2, CH_2, NH + H_2O); ^{13}C NMR ($CDCl_3$) δ 26.54, 27.04, and 28.08 (CH_2), 39.49, 48.45, and 48.63 (NCH_2), 130.16, 131.73, and 151.39 (Ar C), 165.59 (C=O); CI MS, *m/z* 348 (M + 1). Anal. Calcd for $C_{18}H_{29}N_5O_2 \cdot H_2O$: C, 59.15; H, 8.55; N, 19.16. Found: C, 59.80; H, 8.62; N, 19.11.

3,6,10,13,17-Pentaazatricyclo[13.3.1.1^{6,10}]icosa-1(19),15,17-triene-2,14-dione (5a) (19%, mp 210 °C dec): ^1H NMR ($C_6D_5NO_2$, 130 °C) δ 9.12 (br s, 2 H, Ar H), 8.62 (br s, 1 H, Ar H), 7.17 (br, 2 H, NH), 3.69–3.10 (m, 6 H, NCH_2), 2.39–2.94 (m, 8 H, NCH_2), 1.51–1.92 (br m, 2 H, CH_2); ^{13}C NMR ($C_6D_5NO_2$, 100

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°C) δ 25.58 (CH_2), 39.90, 51.29, and 55.21 (NCH_2), 76.93 (NCH_2N), 130.42 and 151.32 (Ar C, one peak is overlapped by the signal of the deuterated solvent), 167.02 (C=O); FAB MS, *m/z* 304 (M + 1). Anal. Calcd for $C_{15}H_{21}N_5O_2 \cdot 0.75H_2O$: C, 56.87; H, 7.11; N, 22.11. Found: C, 57.11; H, 7.19; N, 21.28.

3,7,11,15,19-Pentaazatricyclo[15.3.1.1^{7,11}]docosa-1-(21),17,19-triene-2,16-dione (5b) (37%, mp 228 °C): ^{1}H NMR (DMSO, 135 °C) δ 9.04 (d, 2 H, Ar H), 8.41 (t, 1 H, Ar H), 3.33–3.65 (m, 4 H, NCH_2), 3.20 (s, 2 H, NCH_2N), 2.25–2.88 (m, 8 H, NCH_2), 1.58–2.0 (m, 4 H, CH_2), 1.19–1.58 (m, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 21.75 and 24.85 (CH_2), 41.34, 50.62, and 55.84 (NCH_2), 78.79 (NCH_2N), 129.26, 131.17, and 152.07 (Ar C), 164.54 (C=O); EI MS, *m/z* 331 (M). Anal. Calcd for $C_{17}H_{25}N_5O_2$: C, 61.61; H, 7.60; N, 21.13. Found: C, 61.07; H, 7.72; N, 20.91.

3,8,12,17,21-Pentaazatricyclo[17.3.1.1^{8,12}]tetracosa-1-(23),19,21-triene-2,18-dione (5c) (26%, mp 240 °C dec): ^{1}H NMR ($C_6D_5NO_2$, 130 °C) δ 9.33 (d, 2 H, Ar H), 8.37 (br t, 1 H, Ar H), 8.12 (br, 2 H, NH), 3.41–3.96 (br m, 4 H, NCH_2), 3.20 (s, 2 H, NCH_2N), 2.06–2.84 (br m, 8 H, NCH_2), 1.31–2.04 (br m, 10 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 24.30, 24.45, and 26.35 (CH_2), 39.93, 52.33, and 55.63 (NCH_2), 78.60 (NCH_2N), 128.86, 130.96, and 152.60 (ArC), 165.11 (C=O); EI MS, *m/z* 359 (M). Anal. Calcd for $C_{19}H_{29}N_5O_2 \cdot 0.5H_2O$: C, 61.93; H, 8.20; N, 19.00. Found: C, 61.46; H, 8.48; N, 18.67.

General Procedure for the Cleavage of the CH_2 Group. Macrocycles **5** were converted to **3** by treatment with malonic acid and pyridine in ethanol at reflux temperature for 2 h.[11] The compounds were recrystallized from acetone to give pure **3** (**3a**, 54%; **3b**, 85%; **3c**, 65%). ^{1}H and ^{13}C NMR spectra and mp are identical with those obtained for **3** synthesized in one step from **1** and **2** by the method described above.

Registry No. **1a**, 4741-99-5; **1b**, 4605-14-5; **1c**, 70862-15-6; **2**, 15074-61-0; **3a**, 113431-02-0; **3b**, 113431-03-1; **3c**, 113431-04-2; **4a**, 113431-05-3; **4b**, 113431-06-4; **4c**, 113431-07-5; **5a**, 113431-08-6; **5b**, 113431-09-7; **5c**, 113431-10-0; **6b**, 77215-44-2; $H_2N(CH_2)_3NH_2$, 109-76-2; H_2C=CHCN, 107-13-1; HCHO, 50-00-0; *N,N'*-bis(2-cyanoethyl)-1,3-diaminopropane, 35514-00-2.

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Unexpected Product from Nitration of 1,3-Diethoxybenzene

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Aromatic nitration has been studied very extensively in literature.[1] In this paper we wish to report a novel product obtained from nitration of 1,3-diethoxybenzene. Although nitration of 1,3-dimethoxybenzene[2,3] and 1,4-diethoxybenzene[4,5] give normal mono or dinitro compounds depending on the reaction conditions, we have found that the nitration of 1,3-diethoxybenzene (**1**) leads to the formation of 4-[(2,4-diethoxyphenyl)imino]-3-ethoxy-2,5-cyclohexadien-1-one *N*-oxide in greater than 90% yield. Its structure was fully characterized by elemental analysis,

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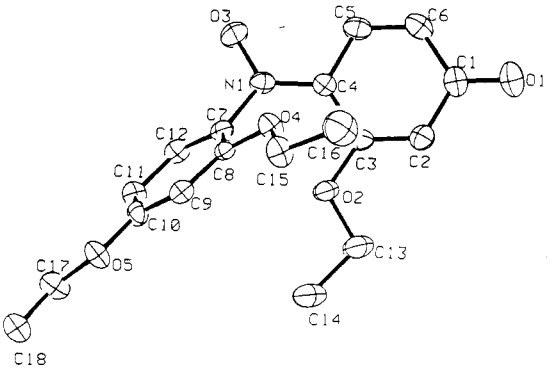
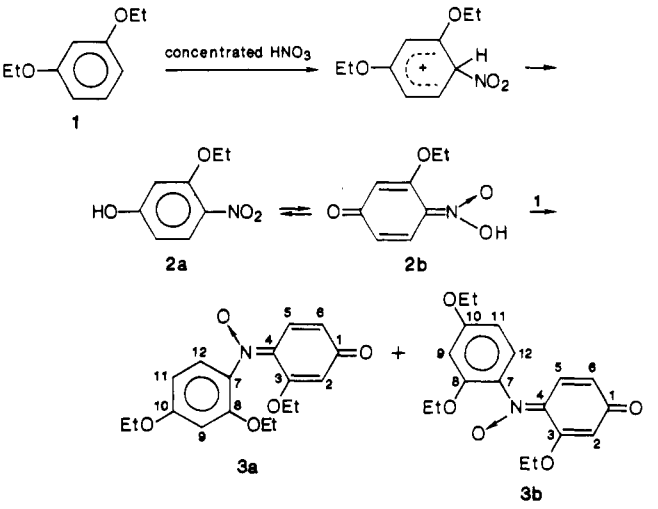


Figure 1. Perspective view of **3a** with numbering of atoms.

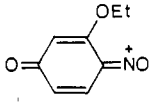
Scheme I



by mass spectrum, which showed a parent peak at mass 331, and by ^{1}H and ^{13}C NMR spectra. The infrared spectrum (KBr) exhibited a strong absorption at 1610 cm^{-1} due to the quinoid carbonyl. The ^{1}H NMR spectrum actually showed it to be a mixture of two isomers **3a** and **3b** in about 97:3 ratio. Table I lists the ^{1}H NMR data including some due to the minor component in the aromatic region. Its absorption is quite similar to that of the abundant component, indicating that they are isomers most likely differing in the orientation of N→O bond.

The X-ray crystal structure and powder diffraction pattern have shown that the abundant isomer (**3a**) is that in which the N→O bond is anti to the OEt group on the quinoid ring (Figure 1). The crystal data also show its benzene ring at a torsion angle of 60° with respect to the quinoid ring. Some of the pertinent X-ray data are summarized in Table II.

Scheme I depicts the formation of these isomers from nitration of 1,3-diethoxybenzene. The difference in its nitration vs that of 1,3-dimethoxybenzene is explained in terms of the formation of **2a**, presumably by olefin elimination from the mononitro product of **1**.[6] Its tautomeric form **2b**, via the cyclohexadiene iminium intermediate,



then reacts with **1** to give **3a** and **3b**. From the overall high yield of the products, it appears that the reaction of **2b**

(6) For a similar nitrosation reaction, see: Hodgson, H. H.; Clay, H. *J. Chem. Soc.* **1930**, 1872.

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