**3b**, 126158-61-0; **3c**, 126158-62-1; **3d**, 118946-84-2; **3e**, 126158-63-2: 3f, 126158-64-3; 3g, 126158-65-4; 3h, 126158-66-5; 3i, 126158-67-6; 3j, 126158-68-7; 3k, 118946-85-3; 3l, 126158-69-8; 3n, 126159-21-5; 4 (Ar = p-MeC<sub>6</sub>H<sub>4</sub>, R = R' = Me), 126158-70-1; 4 (Ar = p-ClC<sub>6</sub>H<sub>4</sub>, R = R' = Me), 118946-86-4; 4 (Ar = p-FC<sub>6</sub>H<sub>4</sub>, R = R' = Me), 126158-71-2; 4 (R, R' =  $CH_2CH_2$ ), 126159-12-4; 4 (R = R' = Ph), 126159-13-5; 4 (R = R' = Me), 94572-63-1; 5, 29411-28-7; 6, 126159-14-6; 7, 126159-15-7; 9, 126159-16-8; 10, 126159-18-0; 11, 126159-17-9; 12, 2450-55-7; 13, 4686-14-0; 14, 6080-60-0; 17b, 126158-80-3; 17c, 126158-81-4; 17d, 126158-82-5; 17f, 126158-83-6; 17g, 126158-84-7; 17h, 126158-85-8; 17i, 126158-86-9; 17n, 126158-87-0; 18, 125879-46-1; 19a, 126159-20-4; 19b, 126158-72-3; 19c, 126158-74-5; 19d, 126158-73-4; 19f, 126158-75-6; 19g, 126158-76-7; 19h, 126158-77-8; 19i, 126158-78-9; 19n, 126158-79-0; 20b, 126158-88-1; 20c, 126158-89-2; 20d, 126158-90-5; 20f, 126158-91-6; 20g, 126158-92-7; 20h, 126158-93-8; 20i, 126158-94-9; 20n, 126158-95-0; 25 (R = 3-OMe), 126158-98-3; 25 (R = 2-OMe), 126158-99-4; 25 (R = 3-Cl), 126159-00-0; 25 (R = 2-Cl), 126159-01-1; 25 (R = 3-Br), 126159-02-2; 25 (R = 3-F), 126159-03-3; 25  $(R = 2, 4-Me_2)$ , 126159-04-4; 25 (R = 3-OMe, 6-Cl), 126159-05-5; 25 (R = H), 2510-61-4; 26 (R = 3-Br), 126159-06-6; 26 (R = 2-OMe), 126159-07-7; 26 (R = 3-Cl), 126159-08-8; 26 (R = 3-F),

126159-09-9; **26** (R = 2,4-Me<sub>2</sub>), 126159-10-2; **26** (R = H), 2510-69-2; t-BuOH, 75-65-0; o-HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 119-36-8; EtO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>Et, 105-53-3; PhCO<sub>2</sub>H, 65-85-0; PhN<sub>3</sub>, 622-37-7; PhCOCN, 613-90-1; p-MeOC<sub>6</sub>H<sub>4</sub>CN, 874-90-8; m-MeOC<sub>6</sub>H<sub>4</sub>CN, 1527-89-5; p-ClC<sub>6</sub>H<sub>4</sub>CN, 623-03-0; m-ClC<sub>6</sub>H<sub>4</sub>CN, 766-84-7; p-BrC<sub>6</sub>H<sub>4</sub>CN, 623-00-7; p-FC<sub>6</sub>H<sub>4</sub>CN, 1194-02-1; p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN, 619-72-7; PhN<sub>3</sub>, 622-37-7; p-ClC<sub>6</sub>H<sub>4</sub>N<sub>3</sub>, 3296-05-7; p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>, 1516-60-5; PhCH<sub>2</sub>NH<sub>2</sub>, 140-29-4; p-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CN, 104-47-2; p-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C(Ph)=C(Ph)CN, 126159-22-6; 3-(4-methoxyphenyl)-4-phenylmaleic anhydride, 104594-83-4; 3-(3-methoxyphenyl)-4-phenylmaleic anhydride, 126158-96-1; 3-(4-methylphenyl)-4-(4-chlorophenyl)maleic anhydride, 126158-97-2; 5chloro-1,4-diphenyl-1,2,3-triazole, 126159-11-3; pinacol, 76-09-5; piperidine, 110-89-4; 3,5-dimethylbenzonitrile, 22445-42-7; 1naphthalenecarbonitrile, 86-53-3; 2-methoxyphenanthrene-9,10dicarboxylic anhydride, 109036-17-1.

Supplementary Material Available: Analytical data for the new compounds listed in Tables III-X, XIII, and XIV and details of the crystal-structure determination of compound 19h (12 pages); structure factors of compound 19h (8 pages). Ordering information is given on any current masthead page.

# Notes

## Reaction of an $\alpha$ -Cyanobenzylidenetriazene with Amines and Related Bases<sup>1</sup>

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3- $(\alpha$ -Cyanobenzylidene)-1-phenyltriazene<sup>2</sup> (1) shows pronounced electrophilic character at the benzylidene carbon and reacts with piperidine to form an  $(\alpha$ -aminobenzylidene)triazene (2e) with loss of cyanide, whereas with aniline it forms an imine of phenylglyoxylic acid, with loss of nitrogen.<sup>3</sup> An analogous difference has been observed between sodium hydroxide, which converts 1 to 1-benzoyl-3-phenyltriazene with loss of cyanide, and alkoxides and phenoxide, which convert 1 to ketals of phenylglyoxylamidine with loss of nitrogen.<sup>3</sup> We report here a brief comparison of other nitrogen bases with the respective reactions of piperidine and aniline.

$$PhN = N - N = C$$

$$PhN = R - R = R' = H$$

$$b: R = CH_3, R' = H$$

$$c: R = R' = CH_3$$

$$d: R = Ph; R' = CH_3$$

$$e: RR' = (CH_2)_5$$

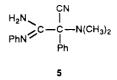
The reactions of 1 with amines were generally spontaneous and mildly exothermic, accompanied in some cases by visible evolution of gas. Ammonia reacted in the same way as piperidine and converted 1 to 2a (or a tautomer). Support for the structure was obtained by oxidation with permanganate to form 2,5-diphenyl-(2*H*)-tetrazole (3) (eq 1).

$$1 \longrightarrow 2a \xrightarrow{KMnO_4} Ph - N \xrightarrow{N \rightarrow Ph} (1)$$

Methylamine gave two products, one corresponding to that formed by ammonia, piperidine, and hydroxide, the other (4a) related to that formed by alkoxide and phenoxide and aniline (eq 2).

1 
$$\xrightarrow{CH_3NH_2}$$
 2a and  $\xrightarrow{H_2N}_{Ph-N}C-C \stackrel{NR}{\stackrel{Ph}{=}} Ph$  (2)  
4a: R = CH<sub>3</sub>  
b: R = NH<sub>2</sub>  
c: R = OH

Dimethylamine also gave two products, in a ratio of ca. 2.5:1: a yellow triazene (2c) and a colorless, new type of compound, 5, which had acquired the elements of HCN.



In an experiment conducted in the presence of an excess of added HCN, the ratio was about 1:2. The HCN required for forming 5 in the first experiment may have come from that released in the formation of 2. Hydrolysis of 5 was accomplished with alcoholic alkali; aniline and benzoic acid were produced.

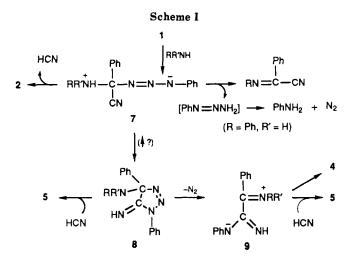
N-Methylaniline reacted incompletely and only with heating and converted 1 to 2d. In contrast, hydrazine

<sup>(1)</sup> From the Senior Honors thesis of G.D.M.

<sup>(2)</sup> Smith, P. A. S.; Krbechek, L. O.; Resemann, W. J. Am. Chem. Soc. 1964, 86, 2025.

<sup>(3)</sup> Smith, P. A. S.; Friar, J. J.; Resemann, W.; Watson, A. C. J. Org. Chem., preceding paper in this issue.

<sup>(4)</sup> Phenyltriazene decomposes spontaneously to aniline and nitrogen: Dimroth, O. Ber. Dtsch. Chem. Ges. 1907, 40, 2376.



reacted very quickly and completely, and converted 1 solely to the hydrazone 4b and, similarly, hydroxylamine converted 1 into the oxime 4c.

Formation of triazenes (3) or  $\alpha$ -imino nitriles may be considered to proceed by addition to the C=N bond of 1, followed by elimination of HCN or phenyltriazene, respectively, whereas formation of amidines (4 and 5) is a more deep-seated change. The latter involves transfer of the anilino group from its attachment to nitrogen to the carbon of the erstwhile cyano group. The most obvious path is through cyclization of an intermediate (7) to form a triazoline<sup>5</sup> (8), as shown in Scheme I. The productdetermining step must consist of competition between cyclization of 7 (or, if  $7 \rightarrow 8$  is reversible, fragmentation of 8) and elimination of HCN. The dipolar intermediate 9 can tautomerize to structure 4 only when R' = H. When it cannot tautomerize, it may then react with available HCN to form 5 (4a did not react with HCN under the conditions of the experiment). The competition between formation of 2 or 4 and 5 is evidently closely balanced, and no simple correlation with basicity of the amine or steric requirements is apparent. There is a close parallel with the reactions of 1 with oxygen nucleophiles, but there are differences in the type of final product (no geminal diamines analogous to ketals are observed).

The foregoing reactions may have preparative value for the multifunctional structures that they give rise to, which are not readily accessible by other means.

#### **Experimental Section**

<sup>1</sup>H NMR spectra were recorded with tetramethylsilane internal reference with a Varian Model A-60 spectrometer. Analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI. Ultraviolet spectra were obtained on a Cary Model 11 spectrometer. Melting points are uncorrected.

**Reaction of 1 with Ammonia.** A solution of 1 (2.34 g, 10 mmol) in 15 mL of redistilled N,N-dimethylacetamide (DMA) was treated dropwise with a solution of 0.7 mL of 15 M aqueous ammonia dissolved in 4 mL of DMA. Slow gas evolution took place. After 8 h, the red solution was saturated with water (odor of HCN), and the mixture was allowed to stand overnight at 5 °C. A yellow-orange solid was filtered off, washed once with DMA/water mixture, and triturated with  $2 \times 5$  mL of water. Recrystallization from 1:1 ether/dichloromethane was accomplished by drying (MgSO<sub>4</sub>), filtering, saturating with petroleum ether (bp 30-40 °C), and cooling to 0 °C. The resulting yellow powder (2a) was washed with several portions of ether and sucked

dry: 0.59 g (26% of **2a**; mp 181–182 °C;  $\lambda_{max}$  (CH<sub>3</sub>OH) 237 nm ( $\epsilon$  = 7260), 342 ( $\epsilon$  = 15000).

The same compound was isolated in 52% yield from 1 (10 mmol) in ether (75 mL) after treatment with 5 mL of 2.0 M anhydrous ammonia in ether. In neither experiment could any other crystalline substances be isolated. Anal. Calcd for  $C_{13}H_{12}N_4$ : C, 69.63; H, 5.40; N, 24.98. Found: C, 69.78; H, 5.29; N, 25.02.

Reaction of 1 with Hydrazine. A solution of 1 (0.50 g, 2.1 mmol) in 20 mL of dried (KOH) oxolane (THF) was treated dropwise during 1 min with a solution of 0.20 g of 95% hydrazine in 25 mL of dried oxolane. The addition was halted when the red color of 1 was discharged (9.0 mL, 2.25 mmol of N<sub>2</sub>H<sub>4</sub>). The pale yellow solution evolved a stream of gas bubbles when a boiling stick was immersed in it. After 1.5 h, the solution was concentrated to dryness (rotary evaporator), and the product was triturated with ether, filtered off, washed with ether, and sucked dry: 4b, 0.35 g; mp 178.5-180 °C with dec. An additional 10 mg (total yield 71%) of 4b (2-hydrazono-2,N-diphenylacetamidine) was isolated from the filtrate. Anal. Calcd for  $C_{14}H_{14}N_4$ : C, 70.57; H, 5.92; N, 23.51. Found: C, 70.28; H, 6.12; N, 23.68. Recrystallization from ethyl acetate gave an analytical sample:  $C_{14}H_{14}N_4$ ; mp 183-184 °C; IR (Nujol) 3490, 3370, 3260, 1620, 1590, 1550, 1240, 720 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH)  $\lambda_{max}$  272 nm ( $\epsilon$  7770).

**Reaction of 1 with Hydroxylamine.** A mixture of 0.33 g (10 mmol) of hydroxylamine<sup>6</sup> and 10 mL of oxolane was treated over 2 min with 1 (2.34 g, 10 mmol) dissolved in 70 mL of oxolane. The solution became warm, evolved gas, turned pale red, and deposited a precipitate after 5 min. The crystals of 2-(hydrox-yimino)-2,N-diphenylacetamidine were collected and washed twice with ether: 1.27 g; mp 208-209 °C dec. The filtrate was concentrated (rotary evaporator), giving an additional 0.22 g, mp 203.5-204 °C dec. (total yield 62%). The first crop was recrystallized three times from methanol to obtain and analytical sample of 4c: colorless; mp 213.5-214 °C; IR (Nujol) 3450, 3300, 3240, 3160, 1660, 1590, 740, 710, 690 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH)  $\lambda_{max}$  254 nm ( $\epsilon$  12000). Anal. Calcd for C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>O: C, 70.28; H, 5.47; N, 17.56. Found: C, 70.25; H, 5.57; N, 17.70.

Reaction of 1 with N-Methylaniline. A solution of 1 (2.00 g, 8.55 mmol) in 50 mL of reagent-grade benzene and 5.0 mL of N-methylaniline was refluxed for 3 days. The benzene was removed (rotary evaporator), and the resulting oil was chromatographed on alumina with diisopropyl ether, followed by a 1:1 mixture with acetone. The first compound eluted was unchanged N-methylaniline (3.2 g), followed by a red-brown band that gave a red gum (1.00 g). Trituration with ether gave  $3-[\alpha-(N-1)]$ methylanilino)benzylidene]-1-phenyltriazene (2d) as a yellow solid wt 0.40 g; mp 149-151 °C; an additional 0.05 g was isolated from the ether triturant (total yield 7%). The main crop was crystallized twice from ether/ligroin (bp 30-40 °C), giving small yellow platelets: mp 151–151.5 °C; IR (Nujol) 1580, 1530, 1300, 1100, 780, 710 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  3.78 (s, 3 H), 6.3–7.7 (m, 16–17 H) (no change with added  $D_2O$ ). At -40 °C, the singlet at 3.78 was split into at least four parts. Anal. Calcd for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.37; H, 5.74; N, 17.94.

**Reaction of 1 with Dimethylamine.** A solution of 1 (2.0 g, 8.5 mmol) in ether (50 mL) was added slowly to a slurry of ether (50 mL) and 23% aqueous dimethylamine (50 mL). The upper layer was removed and concentrated to an oil, which gave 0.10 g of yellow nodules after about 7 h. Three crystallizations from petroleum ether (bp 90-100 °C) gave 5 as white needles: mp 161-162 °C; IR (KBr) 2230 cm<sup>-1</sup> (weak); NMR (CDCl<sub>3</sub>)  $\delta$  2.43 (s, 6 H), 4.83 (broad, ca. 1-2 H), 6.6-8.0 (10 H). Anal. Calcd for C<sub>17</sub>H<sub>18</sub>N<sub>4</sub>; C, 73.33; H, 6.52; N, 20.13. Found: C, 73.53; H, 6.47; N, 19.98.

The triazene (2c) was isolated from a separate experiment. Compound 1 (2.34 g, 10 mmol) was dissolved in 75 mL of warm disopropyl ether, and the solution was cooled to room temperature. Dimethylamine (4.5 mL of 2.26 M in i- $Pr_2O$ , 10 mmol) was added dropwise with stirring; there was a mild exotherm and the solution became orange. No gas was evolved. The solution was seeded with a few crystals of 2c that had been separated mechanically from an earlier experiment. After several hours, the solvent was decanted from a crop of golden kernels, which were

<sup>(5)</sup> Spontaneous fragmentation of  $\Delta^2$ -1,2,3-triazolines is well documented: Kadaba, P. K.; Stanovnik, B.; Tiler, M. Adv. Heterocycl. Chem. 1984, 37, 329.

<sup>(6)</sup> Hurd, C. D. Inorg. Synth. 1939, 1, 87.

washed with diisopropyl ether: 0.80 g (32%); mp 137-139 °C. Recrystallization from diisopropyl ether and from ether/petroleum ether (bp 30-40 °C) gave an analytical sample: mp 138.5-140 °C; IR (Nujol) 1580, 1570, 1510, 1380, 1260, 1110, 770, 700 cm<sup>-1</sup>; UV (CH<sub>3</sub>OH)  $\lambda_{max}$  231 (inflection,  $\epsilon$  6580), 335 nm ( $\epsilon$  17600) (addition of a few drops of 3.6 M HCl caused a peak to appear at 379 nm, ε 10 000);NMR (CDCl<sub>3</sub>) δ 2.85-3.32 (d, 6 H), 7.3 (m, 10 H) (at 55 °C the doublet collapsed to a singlet at 3.08). Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>: C, 71.40; H, 6.39; N, 22.20. Found: C, 71.51; H, 6.48; N, 22.22.

Concentration of the mother liquors and washings led to crystallization of a conglomerate, wt 1.29 g; analysis by IR and UV-vis of a solution gave the composition 0.45 g of 5 and 0.84 g of 2c. A second crop of conglomerate (0.28 g) was isolated from the liquors; total yield of 5 was 0.56 g (20%) and 1.81 g of 2c (72%).

Reaction of 1 with Dimethylamine in the Presence of **HCN.** Hydrogen cyanide (3 mL, 2 g, 70 mmol) was added to a solution of 1 (2.34 g, 10 mmol) in diisopropyl ether (70 mL) prepared as described above. A 2.26 M solution of dimethylamine in diisopropyl ether was added until the color of 1 had disappeared (6 mL required). Gas evolved slowly from the solution, which was seeded with 5 and allowed to stand at 25  $^{\circ}C$  and then at 5 °C. The large cubes that formed were washed with diisopropyl ether: wt 1.30 g. The mother liquor and washings were concentrated to give 1.40 g of a conglomerate; analysis by IR and UV-vis indicated the composition 0.97 g of 2c (38%) and 0.43 g of 5 (total yield 63%).

Reaction of 1 with Methylamine. Conditions similar to those for the reaction of 1 with dimethylamine produced mixtures of 2b and 4a from 1 and methylamine. Compound 4a was isolated from the reaction of 2.0 g (8.5 mmol) of 1 added to an excess of a wet solution of methylamine (obtained by adding NaOH pellets to a mixture of ether and commercial 40% aqueous methylamine). The mixture was cooled in ice for about 1 h, and the white product, 2-(methylimino)-2,N-diphenylacetamidine (4a), was collected, washed with ether, and recrystallized from diisopropyl ether. The somewhat sensitive material was obtained analytically pure after four crystallizations from oxolane/petroleum ether followed by one from acetone: mp 141–141.5 °C with slight dec; NMR (CDCl<sub>3</sub>)  $\delta$  3.25-3.48 (3 H), 5.0 (broad s, 1 H), 7.2-7.85 (m, 10 H) (at 58 °C, the 3.25-3.48 signal collapsed to a singlet at 3.28, and the others appeared at  $\delta$  5.4 and 7.3). 3-[ $\alpha$ -(Methylamino)benzylidene]-1-phenyltriazene (2b) (or a tautomer) was isolated from a reaction of 1 (2.34 g, 10 mmol) in 15 mL of dimethylacetamide (DMA) treated dropwise with 0.8 g of 40% aqueous methylamine (10 mmol) in an equal volume of DMA. Each drop caused immediate gas evolution and warming. After 15 min, the red solution was saturated with water and scratched, giving a precipitate of fine yellow needles. They were washed sparingly with 1:1 aqueous DMA and triturated twice with water and dried in air: 1.21 g; mp 148-151.5 °C dec. Crystallization from ether at 0 °C gave 0.89 g of yellow crystals, homogeneous by TLC: mp 161-162 °C. The original filtrate yielded an additional 0.15 g of impure 2b, mp 118-127 °C (total yield 43%). Four recrystallizations from ether gave an analytical sample: mp 162-163 °C; IR (Nujol) 3260, 1615, 1590, 1570, 1535, 1470, 1430, 1110, 780, 775, 710, 700 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) § 3.03-3.10 (d, 3 H), 6.22 (broad, 1 H), 7.1–7.6 (m, 10 H); UV ( $\dot{C}H_3OH$ )  $\lambda_{max}$  230 (inflection) ( $\epsilon$  8040), 328 nm ( $\epsilon$  16 600); UV in presence of HCl,  $\lambda_{max}$  236 ( $\epsilon$  6900), 310 nm ( $\epsilon$  11 600). Anal. Calcd for  $C_{14}H_{14}N_4$ : C, 70.57; H, 5.92; N, 23.51. Found: C, 70.52; H, 5.92; N, 23.83.

Oxidation of 2a. A sample of 2a (0.50 g, 2.1 mmol) was added in portions to a boiling solution of 0.23 g (1.5 mmol) of potassium permanganate in 1.5 mL of 1.0 M sodium hydroxide and 20 mL of water. The color was discharged before all of the 2a had been added, so further portions of permanganate (3.0 g total) were added. After refluxing for 5 h, the mixture was treated with sodium bisulfite and 300 mL of water was added. The mixture was distilled until about 150 mL of distillate had been collected. The condenser was rinsed with ether to remove product adhering to the walls, and the ether was allowed to evaporate. The dry sticky solid weighed 40 mg (8%). Sublimation (130 °C, 45 Torr) gave colorless needles, mp 101.5-103 °C, not depressed by mixture with authentic 2,5-diphenyltetrazole (3) prepared from phenyl azide and benzaldehyde phenylhydrazone.<sup>7</sup>

Hydrolysis of 5. A solution of 5 (0.45 g, 160 mmol), 10 mL of 25% sodium hydroxide solution, and 5 mL of ethanol was refluxed for 36 h, cooled, and filtered from inorganic solids. After standing overnight at 5 °C, it was again filtered and then acidified with aqueous hydrochloric acid to a thymolphthalein end point. Inorganic solids were filtered off, and the filtrate was acidified (HCl) and concentrated slightly (aspirator, steam bath). The solid that formed was collected and washed with water: 90 mg (46%; mp 121.5-122 °C; IR identical with that of benzoic acid).

A similar reaction was carried out with 0.64 g of 5, and the solvents were decanted from a small amount of a red oil at the end of the refluxing. The oil was taken up in ether and kept for 3 days at 0 °C. The liquid was decanted from a small amount of solid and was then extracted with 5 mL of 15% aqueous HCl. Addition of bromine water precipitated a small amount of 2,4,6-tribromoaniline: mp 119-120 °C; IR identical with that of an authentic sample.

Registry No. 1, 95980-52-2; 2a, 125879-46-1; 2b, 125879-53-0; 2c, 125879-51-8; 3, 18039-45-7; 3d, 125879-49-4; 4a, 125879-52-9; 4b, 125879-47-2; 4c, 125879-48-3; 5, 125879-50-7; PhCO<sub>2</sub>H, 65-85-0; PhNHMe, 100-61-8; HCN, 74-90-8; 2,4,6-tribromoaniline, 147-82-0.

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### Preparation of Triaza-, Tetraaza- and Peraza-Crown Compounds Containing Aminoalkyl Side Groups or Unsubstituted Ring Nitrogen Atoms

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There is interest in the preparation of functionalized macrocyclic ligands. Much of the interest concerns the medical application of complexed metal ions and new metal ion separation techniques. Medicinal applications include the treatment of kidney stones<sup>1</sup> and as nuclear magnetic resonance contrast agents for antibody labeling in cancer diagnosis and therapy.<sup>2-9</sup> Macrocyclic ligands bonded to silica gel can be used to separate specific groups of metal ions.<sup>10,11</sup> From a synthetic point of view, macrocycles containing reactive functional groups are important for the above-listed applications. For example, the

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