A General Procedure for the Syntheses of *N*-Alkyl- and *N*-Aryl-dineopentylamines

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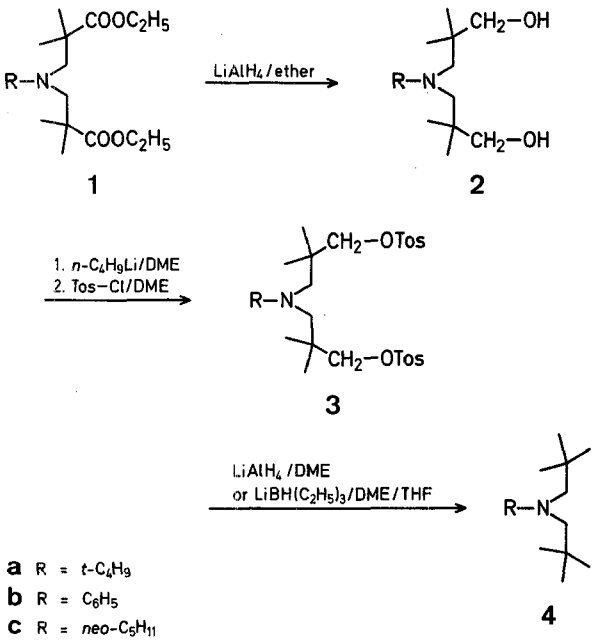
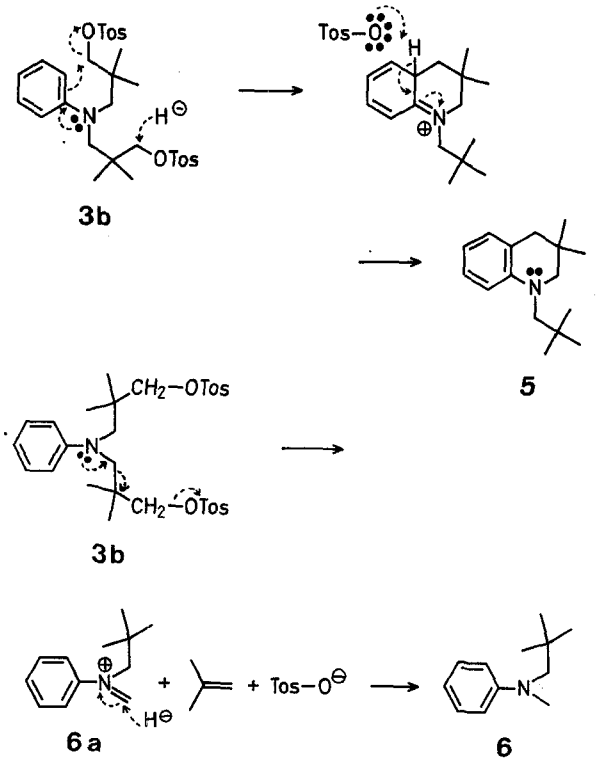
We previously reported on the syntheses and interesting properties of the hindered amino-diesters **1a–c**[1,2]. We now find that these diesters represent good precursors for the syntheses of highly hindered dineopentylamines such as *t*-butyldineopentylamine, *N*,*N*-dineopentylaniline, as well as trineopentylamine[3]. An outline of our general procedure, starting from diesters **1** is shown below[4].



a R = *t*-C_4H_9
b R = C_6H_5
c R = *neo*-C_5H_{11}

While the reactions involving the *N*-alkyl series gave only the desired products[4], the reduction of the *N*-aryl compound **3b** gave several products whose distribution depended on the reaction conditions. For example, reduction of **3b** with lithium aluminum hydride in refluxing 1,2-dimethoxyethane gave approximately a 1:1 mixture of the aniline **4b** and the cyclic amine **5**. A small amount (less than 10% of the mixture) of *N*-methyl-*N*-neopentylaniline (**6**) was also isolated from this reduction. Cyclic amine **5** was presumably formed via an intramolecular displacement reaction and amine **6** via a process involving loss of isobutylene and subsequent reduction of the generated imonium ion **6a**.

When a more active reducing agent, lithium triethylborohydride, was used with refluxing tetrahydrofuran as the solvent, the ratio **4b**:**5** increased to 2:1. This reaction also allowed for much shorter reaction times.



Synthesis of Amino-diols 2a–c; General Procedure:
The amino-diester was added dropwise at 25° to a stirred suspension of lithium aluminum hydride (25% excess active H) in freshly dried ether and the mixture refluxed for 48 h. After the excess lithium aluminum hydride was destroyed with moist ether, the mixture was continuously extracted with ether for 24 h. The organic layer was then dried with potassium carbonate, and the ether removed in vacuo. The crude *N*-*t*-butyl-diol **2a** was distilled and solidified upon standing. The *N*-phenyl- and *N*-neopentyl-diols were purified by sublimation.

N-t-Butyl-3,3'-imino-2,2,2',2'-tetramethyldipropanol (**2a**); yield: 4.16 g (86%); m.p. 42–44°.

$C_{14}H_{31}NO_2$	calc.	C 68.57	H 12.73	N 5.71
(245.4)	found	68.71	12.84	5.64

I.R. (CCl_4): ν_{max} = 3650, 3350, 2960, 2870, 1480, 1398, 1365, 1190, 1050 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 1.97 (s, 12H), 1.12 (s, 9H), 2.62 (s, 4H), 3.40 (s, 4H), 5.10 ppm (s, 2H).

Mass Spectrum (70 eV): *m/e* = 245 (M^+), 242, 228, 182, 172, 144, 142, 116, 100, 86, 72, 56.

N-Phenyl-3,3'-imino-2,2,2',2'-tetramethyldipropanol (**2b**); yield: 2.6 g (85%); m.p. 66–67.5°.

$C_{16}H_{27}NO_2$	calc.	C 72.41	H 10.25	N 5.28
(265.4)	found	72.23	10.18	5.20

I.R.(CCl_4): ν_{max} = 3640, 3350, 2960, 2870, 1595, 1500, 1472, 1040 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 0.82 (s, 12H), 3.22 (s, 4H), 3.30 (s, 4H), 6.9 ppm (m, 5H).

Mass Spectrum (70 eV): *m/e* = 265 (M^+), 234, 192, 174, 148, 120, 106, 77, 57, 55, 44, 41 with a metastable ion at 75.2.

N-Neopentyl-3,3'-imino-2,2,2',2'-tetramethyldipropanol (**2c**); yield: 1.0 g (84%); m.p. 55–58°.

$C_{15}H_{33}NO_2$	calc.	C 69.45	H 12.82	N 5.40
(259.4)	found	69.65	12.92	5.28

I.R. (CCl_4): ν_{max} = 3645, 3450, 3280, 2960, 2870, 2720, 1475, 1400, 1365, 1075, 1052 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 0.93 (s, 12H), 1.1 (s, 9H), 2.25 (s, 2H), 2.38 (s, 4H), 3.4 ppm (s, 4H).

Mass Spectrum (70 eV): *m/e* = 259 (M^+), 244, 228, 202, 186, 130, 114, 58, 57, 56, 55, 45, 44.

Synthesis of the Bis[2,2-dimethyl-3-tosyloxypropyl]-amines 3a–c: General Procedure:
A 10% excess (2.2 mol equiv) of butyllithium was added to a stirred solution of freshly dried 1,2-dimethoxyethane and amino-diol at −78°. Freshly purified tosyl chloride[5] (2.2 mol equiv), dissolved in dry 1,2-dimethoxyethane, was added dropwise to the solution which was allowed to warm to room temperature and stirred for 24 h. The mixture was poured into cold aqueous sodium hydrogen carbonate and the aqueous layer washed with ether. The organic layer was dried with magnesium sulfate and the ether removed in vacuo. The ditosylate was not purified further but used promptly in the next step.

Synthesis of *N*-Alkyl- and *N*-Aryl-dineopentylamines 4a–c: General Procedures:
Procedure A. A two-fold excess of lithium aluminum hydride was added to a stirred solution of ditosylate **3** in freshly dried 1,2-dimethoxyethane and the mixture stirred at room temperature for 1 h and then heated at reflux for 48 h. The mixture was allowed to cool, and moist ether was added. The organic layer was washed with water and the aqueous phase backwashed with ether. The combined organic layers were dried with potassium carbonate and the solvents removed in vacuo. The crude amine was then distilled under vacuum.

Procedure B. The ditosylate **3** was not isolated from the reaction mixture in which it was formed. Excess lithium triethylborohydride (1 *M* in tetrahydrofuran) was added via syringe to the reaction flask at room temperature and the mixture was heated to 65° for 3 h. The product was isolated as described above. The *N*-alkyl-amines were further purified and characterized as their tetrafluoroborate salts. For example, tetrafluoroboric acid (50%) was added to an ethereal solution of the amine and the mixture cooled. The isolated salts were recrystallized from ethyl acetate/methanol.

t-Butyldineopentylamine (**4a**); yield: 40%, as the tetrafluoroborate, using procedure B; the compound did not melt below 320°.

$C_{14}H_{32}BF_4N$	calc.	C 55.81	H 10.72	N 4.65
(301.2)	found	55.66	10.69	4.62

^{1}H-N.M.R. (CCl_4): δ = 0.96 (s, 18H), 1.03 (s, 9H), 2.45 ppm (s, 4H).

Mass Spectrum (70 eV): m/e = 213, 198, 156, 142, 100, 72, 71, 57, 56, 55.

N,N-Dineopentylaniline (**4b**); yield: 49% (by G.L.C.); isolated after separating as a solid (m.p. 32–34°) from a distilled mixture of **4b**, **5**, and **6** (b.p. of mixture: 66–68°/0.03 torr).

$C_{16}H_{27}N$	calc.	C 82.36	H 11.66	N 6.00
(233.4)	found	82.18	11.59	5.86

I.R. (CCl_4): ν_{max} = 2960, 1595, 1500, 1475, 1362, 1200, 1140 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 0.80 (s, 18H), 3.25 (s, 4H), 6.92 ppm (m, 5H).

Mass Spectrum (70 eV) *m/e* = 233 (M^+), 218, 176, 106, 91, 77, 71, 55, 43, with a metastable ion at 64.0.

3,3-Dimethyl-1-neopentyl-1,2,3,4-tetrahydroquinoline (**5**); this product solidified after purification by G.L.C.; yield: 26% (by G.L.C.); m.p. 48–49°.

$C_{16}H_{25}N$	calc.	C 83.06	H 10.89	N 6.05
(231.4)	found	82.95	10.67	5.93

I.R. (CCl_4): ν_{max} = 2960, 2870, 1605, 1495, 885 m^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 1.02 (s, 15H), 2.46 (s, 2H), 2.92 (s, 2H), 3.00 (s, 2H), 6.45 ppm (m, 4H).

Mass Spectrum (70 eV): *m/e* = 231 (M^+), 216, 174, 160, 146, 145, 144, 143, 132, 118, 91.

N-Methyl-N-neopentylaniline (**6**):

I.R. (CCl_4): ν_{max} = 2960, 1600, 1250, 860 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 0.82 (s, 9H), 2.82 (s, 3H), 3.01 (s, 2H), 6.9 ppm (m, 5H).

Mass Spectrum (70 eV): *m/e* = 177 (M^+), 176, 119, 105, 104, 103, 76.

Trineopentylamine (**4c**); yield: 35% (as the tetrafluoroborate) using procedure B; m.p. 221–223°.

Spectra of **4c** agreed in all respects to those reported[3].

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[1] P. Y. Johnson, I. Jacobs, *Chem. Commun.* **1972**, 925.

[2] Presented in part at the Fifth Northeast Regional American Chemical Society Meeting, Rochester, N.Y., 1973.

[3] This compound was synthesized in a clever, but not generally applicable manner while our studies were nearing completion; see W. T. Ford, *J. Org. Chem.* **38**, 3614 (1973).

[4] Amines **1b** and **1c** were synthesized by the same general procedure used to make **1a** (see Ref. 1). Details of their properties including low-temperature ^{1}H- and ^{13}C-N.M.R. spectra will be published in a forthcoming paper.

[5] L. Fieser, M. Fieser, *Reagents for Organic Synthesis*, Vol. I, John Wiley & Sons, New York, 1967, p. 1180.