Design and Synthesis of Two Aromatic Amines with Dendritic Structure

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The design and synthesis of two aromatic amines with dendritic structures, *i.e*. 3,4,5-tribenzyloxyaniline (3,4,5-G_1-NH_2) and 2,5-dibenzyloxyaniline (2,5-G_1-NH_2), were conducted. A coupling reaction of three or two equivalents of benzyl bromide to one equivalent of methyl hydroxybenzoate generated methyl 3,4,5-tribenzyloxybenzoate (3,4,5-G_1-$COOCH_3$), methyl 2,5-dibenzyloxybenzoate (2,5-G_1-$COOCH_3$) and 2,6-dibenzyloxybenzoate (2,6-G_1-$COOCH_3$) in high yields. All G_1-$COOCH_3$ derivatives were studied by X-ray analysis. The results show that these dendrons have sufficient volume to be used as the fine ligands for certain catalysts. The amide intermediates (benzamide, G_1-$CONH_2$) were obtained by reaction between ammonia and G_1-$COOCH_3$. Interestingly, 2,6-dibenzyloxybenzamide (2,6-G_1-$CONH_2$) can not be prepared in the same condition, which may be due to the overlarge steric block. Sodium hypochlorite was an effective oxidant to generate methyl carbamates G_1-$NHCO_2CH_3$.

Keywords aromatic amine, dendritic structure, Hofmann rearrangement

Introduction

Aromatic amines are important synthetic intermediates that play a central role in many areas such as polymer and medicine,[1-4] which can be produced by the reduction of the corresponding nitro aromatic with a metallo hydride reagent or by catalytic hydrogenation.[5] The selective reduction of aromatic nitro groups in the presence of sensitive functional groups, *e.g*. carbonyl, cyano, chloro and alkenic groups, with hydrogen is usually difficult, because these sensitive functionalities are reduced faster with hydrogen than the nitro group.[6] Furthermore, the above reduction in the presence of sensitive functional groups produces sub-pollution along with the need for rigorous reaction conditions.[6] Comparatively, Senanayake *et al*. found that the conversion of aliphatic amides into amines with various oxidants was an effective alternative to the above mentioned method.[7]

In this paper, we reported the mild synthesis via Hofmann rearrangement and characterization of such aromatic amines with dendritic structures. These amines have potential values in many fields owing to their structural features, such as self-assembled supramolecular dendrimers,[8-10] novel catalyst capping metal nanoparticles,[11] and side-chains in polymers.[12] Two types of aromatic amines with dendritic structures, *i.e*., 3,4,5-tribenzyloxyaniline (3,4,5-G_1-NH_2) and 2,5-dibenzyloxyaniline (2,5-G_1-NH_2), were described in this paper.

Experimental

All experiments were carried out under an atmosphere of nitrogen. The solvent *N*,*N*-dimethylformamide was dried on molecular sieves of 4 Å. Elemental analyses (C, H, N) were performed on a VarioEL III elemental analyzer. Mass spectra were recorded by a Finnigan MAT LCQ^{TM} mass spectrometer equipped with an electrospray ionization source. NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument with deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal reference.

Methyl 3,4,5-trihydroxybenzoate was purchased from Acros Organics Co., methyl 2,5-dihydroxybenzoate from Aldrich Chemical Co. and methyl 2,6-dihydroxybenzoate from Tokyo Chemical Industry Co. All other chemicals were obtained commercially and used as received unless stated otherwise.

General procedure for the synthesis of G_1-$COOCH_3$

Methyl 3,4,5-tribenzyloxybenzoate (3,4,5-G_1-$COOCH_3$) was prepared according to the reference.[13] Methyl 3,4,5-trihydroxybenzoate (0.01 mol) and dried potassium carbonate (0.04 mol) were sequentially added into a 150 mL three-neck bottle. As *N*,*N*-dimethylformamide (40 mL) was added into the bottle, sequent benzyl bromide (0.034 mol) was added dropwise into the solution above. After being stirred at 50 ℃ for 24 h, the resultant mixture was allowed to be cooled in ice water.

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After removal of the solvent, the residue was chromatographed on silica gel with ethyl acetate/petroleum ether solution as the eluent to obtain white powder in 91% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40—7.25 (m, 17H, ArH), 5.14 (s, 4H, $ArCH_2O_m$), 5.11 (s, 2H, $ArCH_2O_p$), 3.89 (s, 3H, CO_2Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.3, 152.2, 142.0, 137.1, 136.3, 128.2, 127.8, 127.7, 127.6, 127.2, 124.9, 108.7, 74.8, 70.9, 51.9; IR (KBr) v: 3030, 2946, 2876, 2000—1700, 1750—1725, 1714, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 454 (M^+). Anal. calcd for $C_{29}H_{26}O_5$: C 76.63, H 5.77; found C 76.46, H 5.94.

The preparation procedures of methyl 2,5-dibenzyloxybenzoate (2,5-G_1-$COOCH_3$) and methyl 2,6-dibenzyloxybenzoate (2,6-G_1-$COOCH_3$) were similar to that of 3,4,5-G_1-$COOCH_3$. Finally, 2,5-G_1-$COOCH_3$ was obtained as white powders in 87% yield. ^{1}H NMR ($CDCl_3$, 400 MHz,) δ: 7.37—6.93 (m, 13H, ArH), 5.11 (s, 2H, $ArCH_2O_o$), 5.03 (s, 2H, $ArCH_2O_m$), 3.90 (s, 3H, CO_2Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.6, 152.6, 137.0, 136.8, 128.6, 128.5, 128.1, 127.8, 127.6, 127.0, 121.6, 120.4, 117.2, 116.4, 71.9,70.7, 52.1; IR (KBr) v: 3030, 2946, 2876, 2000—1700, 1750—1725, 1714, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 348 (M^+). Anal. calcd for $C_{22}H_{20}O_4$: C 75.84, H 5.79; found C 75.40, H 5.89. 2,6-G_1-$COOCH_3$ was obtained as white powders in 82% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38—7.29 (m, 10H, Ph), 7.20 (t, J=8 Hz, 1H, ArH), 6.59 (d, J=8 Hz, 2H, ArH), 5.12 (s, 4H, $ArCH_2O$), 3.89 (s, 3H, CO_2Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.9, 156.5, 136.8, 131.0, 128.5, 127.8, 126.9, 114.3, 105.9, 70.5, 52.3; IR (KBr) v: 3030, 2946, 2876, 2000—1700, 1750—1725, 1714, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 348 (M^+). Anal. calcd for $C_{22}H_{20}O_4$: C 75.84, H 5.79; found C 75.66, H 5.95.

General procedure for the synthesis of G_1-$CONH_2$

A stirred solution of 3,4,5-G_1-CO_2CH_3 (3.06 mmol) in ethanol (200 mL) was heated approximately to 100 ℃. Ammonia gas was bubbled through the mixture for 30 h, which was then cooled to room temperature overnight. The separated solid was collected by filtration and washed with water to generate 3,4,5-tribenzyloxybenzamide (3,4,5-G_1-$CONH_2$) as white needles (1.10 g, 76.4%); ^{1}H NMR ($CDCL_3$, 400 MHz) δ: 7.33—7.23 (m, 15H, ArH), 7.10 (s, 2H, ArH), 5.84 (br, 1H, NH), 5.63 (br, 1H, NH), 5.13 (s, 4H, $ArCH_2O_m$), 5.07 (s, 2H, $ArCH_2O_p$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 168.8, 152.8, 141.8, 137.4, 136.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.5, 107.4, 75.2, 71.5; IR (KBr) v: 3340, 3325, 2876, 2000—1700, 1770—1710, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 439 (M^+). Anal. calcd for $C_{28}H_{25}NO_4$: C 76.54, H 5.69, N 3.19; found C 76.44, H 5.63, N 3.25.

A stirred solution of 2,5-G_1-CO_2CH_3 (3.62 mmol) in ethanol (100 mL) was heated approximately to 80 ℃. Ammonia gas was bubbled through the mixture for 4 h, which was then cooled to room temperature. The solution was then extracted with dichloromethane (50 mL×3). The filtrate was concentrated, washed with water, and dried in vacuum to generate 2,5-dibenzyloxybenzamide (2,5-G_1-$CONH_2$) as white powder (1.15 g, 95.5%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.89 (d, J=8 Hz, 1H, ArH), 7.84 (br, 1H, NH), 7.45—7.30 (m, 10H, ArH), 7.10 (br, 1H, ArH), 7.01 (d, J=8 Hz, 1H, ArH), 5.69 (br, 1H, NH), 5.14 (s, 2H, $ArCH_2O$), 5.08 (s, 2H, $ArCH_2O$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 166.6, 153.2, 151.6, 136.9, 135.8, 129.0, 128.7, 128.6, 128.0, 127.9, 127.6, 121.8, 121.0, 117.0, 114.5, 72.0, 70.6; IR (KBr) v: 3340, 3325, 2876, 2000—1700, 1770—1710, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 333 (M^+). Anal. calcd for $C_{21}H_{19}NO_3$: C 75.68, H 5.71, N 4.20; found C 75.82, H 5.32, N 4.15.

General procedure for the synthesis and purification of G_1-NH_2

A solution of NaOH (20 mmol) in MeOH (150 mL) was cooled approximately to 4 ℃. 7 mL of 9% NaOCl (Chlorox) plus carboxamide 3,4,5-G_1-$CONH_2$ (2.0 mmol) was added into this magnetically stirred mixture, with the former being added drop-wise. The mixture was allowed to be warmed to room temperature and then stirred intensively for 30 min to produce the intermediate carbamate 3,4,5-G_1-$NHCO_2CH_3$. A solution of NaOH (40 mmol) in MeOH (10 mL) and water (2 mL) was added, and the whole mixture was heated under reflux for 4 d. The obtained solution was cooled to room temperature and then the solvent was evaporated in vacuum to separate out the precipitate. The precipitate was removed by filtration, the filtrate concentrated, and the separated solid collected by filtration and washed with water to give amine 3,4,5-G_1-NH_2 as pale yellow powder (0.62 g, 75.3%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.42—7.27 (m, 15H, ArH), 6.99 (s, 2H, ArH), 5.05 (s, 4H, $ArCH_2O_m$), 4.96 (s, 2H, $ArCH_2O_p$), 3.48 (br, 2H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 153.5, 142.7, 138.2, 137.3, 128.7, 128.5, 128.5, 128.1, 128.1, 127.8, 127.7, 127.4, 95.6, 75.5, 71.1; IR (KBr) v: 3350, 3300, 2870, 2000—1700, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 411 (M^+). Anal. calcd for $C_{27}H_{25}NO_3$: C 78.83, H 6.08, N 3.41; found C 78.93, H 6.54, N 3.67.

2,5-G_1-NH_2 was prepared from 2,5-G_1-$CONH_2$ (3 mmol), similarly to 3,4,5-G_1-$CONH_2$. A pale yellow solid (0.79 g, 86%) was obtained. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43—7.28 (m, 10H, ArH), 6.76 (d, J=8 Hz, 1H, ArH), 6.42 (d, J=8 Hz, 1H, ArH), 6.30 (br, 1H, ArH), 5.01 (s, 2H, $ArCH_2O$), 4.98 (s, 2H, $ArCH_2O$), 3.84 (br, 2H, NH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 154.0, 141.2, 137.7, 137.5, 137.4, 128.6, 128.5, 128.0, 127.8, 127.6, 127.4, 113.3, 103.3, 103.1, 71.3, 70.4; IR (KBr) v: 3350, 3300, 2870, 2000—1700, 1600, 1587, 1499, 1376, 1300—1200, 1109 cm^{-1}; MS (70 eV) m/z: 305 (M^+). Anal. calcd for $C_{20}H_{19}NO_2$: C 78.69, H 6.23, N 4.59; found C 78.54, H 6.75, N 4.69.

X-ray crystallography

Data were collected at 298 K on a Bruker Smart CCD X-ray diffractometer, fitted with Mo Kα radiation (0.71073 Å). The structure was solved by direct methods. Anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. All crystals of 3,4,5-G_1-$COOCH_3$, 2,5-G_1-$COOCH_3$ and 2,6-G_1-$COOCH_3$ suitable for structural determination by using XRD were grown in a mixed ethyl acetate/petroleum ether (V∶V=1∶2) solution. Crystallographic and refinement parameters are given in Table 1. Supplementary crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC 632789-632791). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 0044-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program used to solve structure: SHELXS97 (Sheldrick, 1997); program used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORETP-3 (Farrugia, 1997) and PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

Table 1 X-ray crystal data for 3,4,5-G_1-$COOCH_3$, 2,6-G_1-$COOCH_3$ and 2,5-G_1-$COOCH_3$

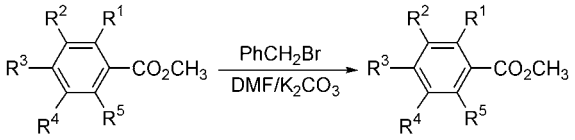
	3,4,5-G_1-$COOCH_3$	2,6-G_1-$COOCH_3$	2,5-G_1-$COOCH_3$
CCDC number	632789	632790	632791
Formula	$C_{29}H_{26}O_5$	$C_{22}H_{20}O_4$	$C_{22}H_{20}O_4$
Formula weight	454.50	348.38	348.38
Crystal color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Triclinic	Monoclinic
Crystal size/mm^3	0.45×0.30×0.30	0.40×0.18×0.13	0.45×0.38×0.28
Space group	$P2_1/n$	P-1	$P2_1/c$
Radiation type	Mo Kα	Mo Kα	Mo Kα
Wavelength/Å	0.71073	0.71073	0.71073
a/Å	11.005(2)	8.859(3)	21.083(5)
b/Å	16.612(3)	14.280(6)	10.724(2)
c/Å	13.350(2)	15.827(6)	7.8762(17)
α/(°)	90	64.208(7)	90
β/(°)	104.956(3)	81.443(7)	93.595(4)
γ/(°)	90	88.815(8)	90
Volume/Å^3	2357.8(7)	1780.4(12)	1777.2(7)
Z	4	4	4
θ range for data collection/(°)	2.20—26.29	2.07—26.00	2.71—28.32
D_{calc}/(Mg•m^{-3})	1.280	1.300	1.302
Absorption coefficient/mm^{-1}	0.087	0.087	0.089
F(000)	960	736	736
Reflections collected	22192	9167	8613
Independent reflections	4141 [R(int)=0.0247]	6197 [R(int)=0.0299]	3109 [R(int)=0.0194]
Data/restraints/parameters	4140/0/307	6197/0/469	3109/0/236
Goodness-of-fit on F^2	1.278	1.063	1.044
Final R indices [$I>2\sigma(I_0)$]	R_1=0.0492	R_1=0.0730	R_1=0.0510
	wR_2=0.1580	wR_2=0.1733	wR_2=0.1609
R indices (all data)	R_1=0.0573	R_1=0.0950	R_1=0.0587
	wR_2=0.1637	wR_2=0.1868	wR_2=0.1750
$\Delta\rho_{max}$/(e•Å^{-3})	0.193	0.191	0.348
$\Delta\rho_{min}$/(e•Å^{-3})	−0.206	−0.199	−0.287

Results and discussion

Preparation of G_1-$COOCH_3$

The convergent dendrimer synthesis described by Hawker and Fréchet is based on the reaction of two equivalents of benzylic bromide and one equivalent of the 3,5-dihydroxybenzyl alcohol monomer.[14] The first generation benzylic alcohol can also be easily prepared in large amounts through a coupling reaction of two equivalents of benzyl bromide to one equivalent of methyl 3,5-dihydroxybenzoate. 3,4,5-G_1-$COOCH_3$, 2,5-G_1-$COOCH_3$ and 2,6-G_1-$COOCH_3$ were prepared (Scheme 1) successfully according to the paper.[13] In practice, the reaction is also Williamson reaction.[13]

Scheme 1 Preparation equation of G_1-$COOCH_3$



3,4,5-G_1-$COOCH_3$
2,5-G_1-$COOCH_3$
2,6-G_1-$COOCH_3$

	R^1	R^2	R^3	R^4	R^5
3,4,5-G_1-$COOCH_3$	H	$PhCH_2O$	$PhCH_2O$	$PhCH_2O$	H
2,5-G_1-$COOCH_3$	$PhCH_2O$	H	H	$PhCH_2O$	H
2,6-G_1-$COOCH_3$	$PhCH_2O$	H	H	H	$PhCH_2O$

Structure of G_1-$COOCH_3$

The molecular structures of the dendrons are shown in Figures 1—3. The two planes of the substitutional *m*-phenyl rings are oriented essentially orthogonally to that of the central phenyl ring (*ca*. 84.6° and 108°, respectively), and the angle is *ca*. 23° between the plane of the substitutional *p*-phenyl ring and the plane of the central phenyl ring (3,4,5-G_1-$COOCH_3$ is depicted in Figure 1). Similarly, the planes of the substitutional phenyl rings which are parallel with each other are approximately perpendicular (*ca*. 80.1°) to that of the central phenyl ring (2,5-G_1-$COOCH_3$ is depicted in Figure 2). There are two different molecular structures in the asymmetric unit of 2,6-G_1-$COOCH_3$, which are shown in Figure 3. It shows that the plane of one substitutional *o*-phenyl ring is approximately on the same plane with the plane of the central phenyl ring (*ca*. 2.5°), between which and the plane of the other substitutional *o*-phenyl ring the angle is *ca*. 70.8° in molecular structure a. Compared with molecular structure a, one substitutional *o*-phenyl ring in molecular structure b is approximately orthogonal to that of the central phenyl ring (*ca*. 93°), between which and the other substitutional plane the angle is *ca*. 52.8°.

From above, we know that these dendrons have very great volumes, due to their dendritic structure features. These bulky dendrons can be used as the fine ligands for certain catalysts, such as Brookhart's catalysts.[15]

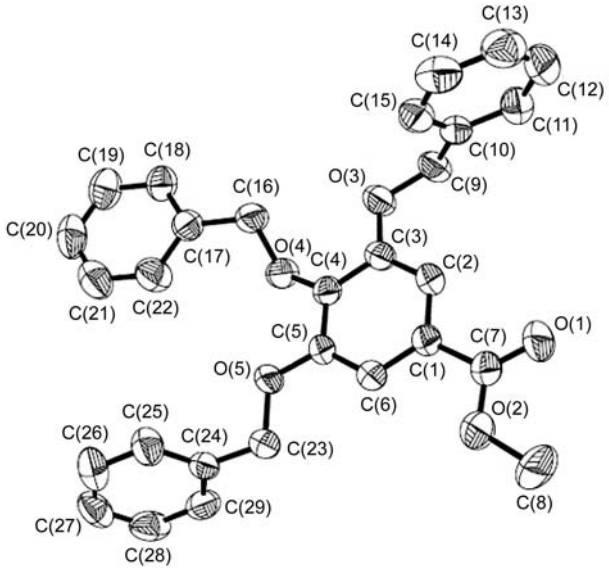


Figure 1 A view of the molecule of 3,4,5-G_1-$COOCH_3$, with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are deleted.

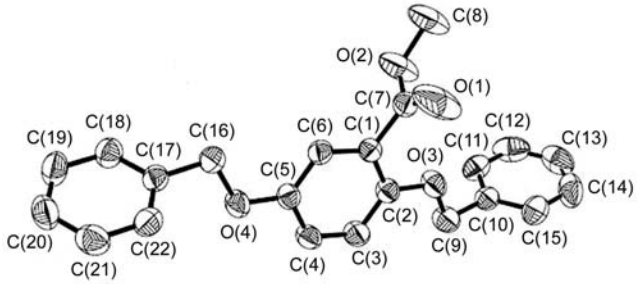


Figure 2 A view of the molecule of 2,5-G_1-$COOCH_3$, with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are deleted.

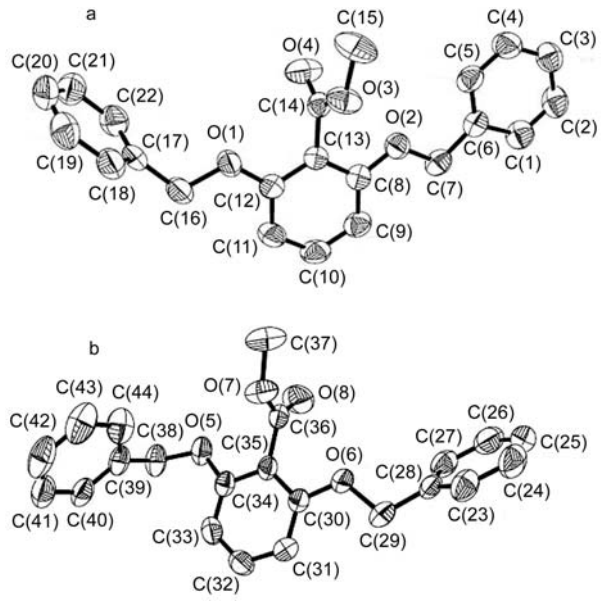


Figure 3 Two views of the molecule of 2,6-G_1-$COOCH_3$, with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are deleted.

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Transformation process of COOMe to NH_2

Classical methods for the transformation of COOMe to NH_2 include the Hofmann[16] and Curtius[17] rearrangement. We have concentrated on the former, and the necessary amide intermediates G_1-$CONH_2$ were prepared by reaction with ammonia. Many variations on the original bromine/aqueous sodium hydroxide rearrangement conditions have been reported. Of particular interest is a method which used sodium hypochlorite in methanol under mild conditions. In the present research, this method worked well to give methyl carbamates G_1-$NHCOOCH_3$, which were hydrolyzed in alkali to liberate the amines G_1-NH_2; the procedure was optimized so that the isolation step of the carbamates was unnecessary.

Ammonolysis

The present process involves a facile method to extremely pure G_1-$CONH_2$. To achieve this, powder G_1-$COOCH_3$ is dissolved in glycol and treated with gaseous ammonia in 80—100 ℃.

Eq. 1 takes place at as low as 1.01×10^5 Pa NH_3 pressure. Depending on the different reaction time, the specific conversions of 3,4,5-G_1-$CONH_2$ ranged from 47.2% to 76.4% (Figure 4). It was shown that the conversion increased as the reaction time increased over the period of 0—24 h, and, a moderate constant conversion was kept from 24 to 48 h. The reaction rate and the selectivity depended decisively on the use of glycol, which acts in two ways: while catalyzing the ammonolysis, it also serves as a very specific solvent in which the starting benzoates as well as the intermediates are soluble but the final product 3,4,5-G_1-$CONH_2$ is insoluble.[18] The 3,4,5-G_1-$CONH_2$ formed is extremely pure and easy to be isolated by filtration.

$$G_1\text{-}COOCH_3 \xrightarrow{NH_3} \text{Intermediate} \underset{P}{\overset{T}{\rightleftharpoons}} G_1\text{-}CONH_2 \qquad (1)$$

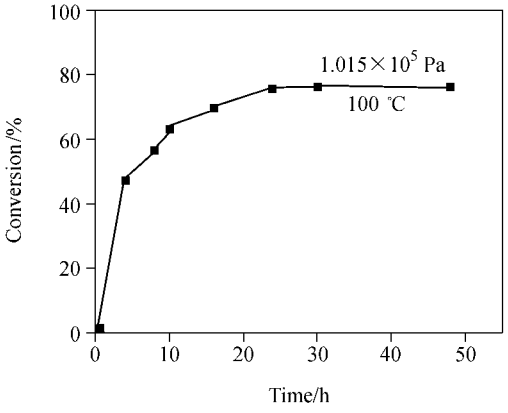


Figure 4 Dependence of 3,4,5-G_1-$CONH_2$ conversion on reaction time.

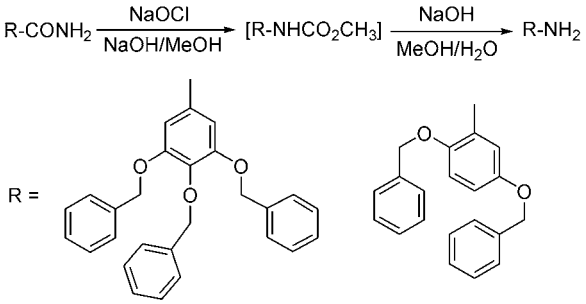
Other than 3,4,5-G_1-$CONH_2$, 2,5-G_1-$CONH_2$ is soluble in glycol. So we obtained 2,5-G_1-$CONH_2$ by extraction with dichloromethane. The yield of 2,5-G_1-$CONH_2$ was higher than 95% of the theoretical quantity. Moreover, only 4 h were needed to accomplish the task.

An interesting thing was that the 2,6-G_1-$CONH_2$ could not be prepared in the same condition, which may be due to the larger steric bulk described above.

Hofmann rearrangement

The classical method for this transformation involves the use of an alkaline solution of bromine, which is, however, unsatisfactory and unreliable.[19] Numerous modifications of this rearrangement have been reported using a variety of oxidants and bases, such as iodine(III) reagents [$PhI(OCOCF_3)_2$,[20] PhI-HCO_2H, PhI(OTs)OH and $PhI(OAc)_2$], lead tetraacetate,[21] (NBS)-$Hg(OAc)_2$,[22] NBS-NaOMe,[23] and NBS-DBU.[24] Herein, we choose sodium hypochlorite (NaOCl) as oxidant (Scheme 2), because it is an inexpensive, convenient and safe alternative to the current employed oxidants.[25]

Scheme 2 Preparation equation of G_1-NH_2



When NaOCl was added to a cold solution of carboxamide 3,4,5-G_1-$CONH_2$ in methanolic NaOH, the solution became pale yellow gradually. The reaction was checked after about 0.5 h thin-layer chromatography (TLC), which revealed the complete disappearance of the starting amide. Work up of the reaction afforded methyl carbamate 3,4,5-G_1-$NHCO_2CH_3$, which was hydrolyzed in alkali to liberate the amines 3,4,5-G_1-NH_2.

Our best results were obtained by the addition of NaOCl (9 equiv.) in one portion to a chilled (4 ℃), stirred solution of the 3,4,5-G_1-$CONH_2$ (1 equiv.) and NaOH (6 equiv.) in methanol. Upon dissolution of the NaOCl, the reaction was stirred for 15 min, followed by removal of the ice-water bath and warming to room temperature. Completion of the reaction was evidenced by TLC, and then another mixed solution (NaOH/MeOH/H_2O) was added to the former solution, which was refluxed for 4 d, then concentrated, filtrated to afford amine 3,4,5-G_1-NH_2 in 75.3% isolated yield. 2,5-G_1-$CONH_2$ was similarly converted to the corresponding amine 2,5-G_1-NH_2 in better yield (86%).

The above reaction probably follows a path similar to the classic Hofmann rearrangement. Under the highly basic reaction conditions, OCl^- is the predominant

form of chlorine, which reacts with the amide to form *N*-chloroamide to undergo a rearrangement to the isocyanate. In the presence of methanol, the isocyanate forms a methyl carbamate, which is hydrolyzed in alkali to liberate the amine.

Conclusion

Two aromatic amines with dendritic structures were successfully synthesised. The X-ray study of G_1-$COOCH_3$ shows that the three dendrons have large but proper volumes as the fine ligands of Brookhart's catalyst. The amides prepared by ammonolysis of G_1-$COOCH_3$ in high yields have been readily converted to the corresponding amines using sodium hypochlorite as the oxidant. Further studies are in progress in our group.

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