Registry No. 1, 1076-38-6; 3, 91739-58-1; 4, 91663-61-5; 7, 116947-03-6; 8, 116947-04-7; 9, 116864-01-8; 10, 116864-02-9; 11, 116864-03-0; 14, 116864-04-1; 15, 95598-16-6; 16, 95598-17-7; 19, 116864-05-2; 20, 116947-05-8; 21, 116864-06-3; 22, 116947-06-9; 23, 116864-07-4; 24, 116864-08-5; 25, 92809-86-4; 26, 116864-09-6; 29, 116864-10-9; 30, 116864-11-0; 31, 116864-12-1; 32, 116947-07-0; 33, 116864-13-2; 2-methyl-2-butene, 513-35-9; isopropenyl acetate, 108-22-5; ethyl vinyl ether, 109-92-2.

Supplementary Material Available: The anisotropic thermal parameters for the non-hydrogen atoms and the coordinates and temperature factors for the hydrogen atoms for compounds 3, 4, and 14 can be found in Tables I–XIV (16 pages). Ordering information is given on any current masthead page.

Notes

Amination of 3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone

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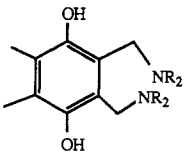
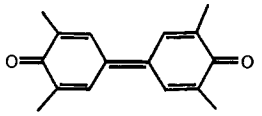
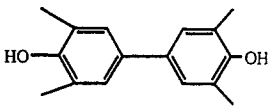
Cameron, Scott, and Todd have reported[1] that fully alkylated quinones, such as duroquinone, readily undergo a novel amination to give the bis(aminomethyl)quinol derivative 1, together with the corresponding tris and tetrakis derivatives. However, Brown and Todd[2] reported earlier that 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (2) reacts with cyclohexylamine, piperidine, or morpholine in air to yield only its reduction product 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (3). Here we report different results from the reaction between 2 and several amines and ϵ-caprolactam.



1

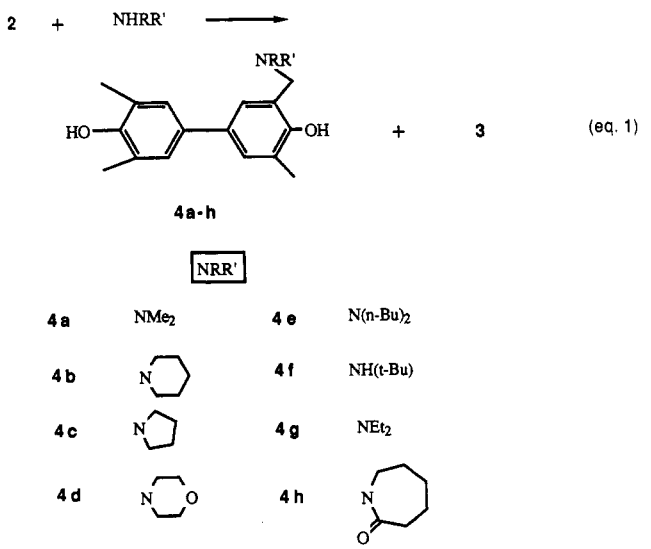


2



3

The reactions of 2 with various amines including dimethylamine, piperidine, pyrrolidine, morpholine, di-*n*-butylamine, *tert*-butylamine, and diethylamine at room temperature gave monoaminated products **4a–g** as the major products (eq 1). Various amounts of reduced diol 3 were the second major component. The bisaminated adducts were usually formed in trace amounts. The best yields of **4a–g** were obtained when the reactions were performed in 1-methyl-2-pyrrolidinone (NMP). No reaction occurred between the weaker nucleophile ϵ-caprolactam and 2 at room temperature in NMP. The adduct **4h** was obtained only after heating for several hours at elevated temperature. The molar ratios of monoadducts **4a–h** to 3 in the reaction mixture are listed in Table I. The yields of monoadduct are in general higher than those of the diol 2 except in the case of morpholine and ϵ-caprolactam, which may be due to the reduced nucleophilicity of the amines. Also, it may be reasoned that the monoadducts **4a–g** are less prone to oxidation to diphenoquinone, the suspected intermediate in the formation of the bisaminated derivative.



No reaction occurred between 2 and di-*n*-butylamine in nonpolar solvents such as toluene and benzene at room temperature. In summary, we found a unique method of preparing mono-*o*-(aminomethyl)biphenyldiol derivatives which were not readily available synthetically.

Experimental Section

Compounds were used as received without further purification, unless otherwise noted. The GC data was obtained from a Shimadzu GC-9A gas chromatograph using a Supelco SPB-5 (30 m, 0.32-mm i.d.) column with a Shimadzu C-R3A integrator. The ratios of each monoadduct **4a–h** to 3, respectively, were obtained from GC after silylation of the reaction aliquot with *N,O*-bis(trimethylsilyl)trifluoroacetamide to prevent the decomposition of **4a–h**. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Perkin-Elmer 598 or a Nicolet 7199 infrared spectrophotometer. NMR spectra were obtained with a Varian EM-390 (^{1}H NMR, 90 MHz) or a Varian XL-300 (^{13}C NMR, 75 MHz) spectrometer relative to an internal tetramethylsilane standard. High-resolution and field-desorption mass spectra were recorded on a Varian MAT 731 mass spectrometer. A Shimadzu UV-240 UV–visible recording spectrophotometer was used for obtaining UV–visible spectral data.

General Procedure for the Synthesis of Compounds 4a–g. To a round-bottom flask with a magnetic stirring bar were added amine (0.1 mol), compound 2 (5.0 g, 0.021 mol), and 100 mL of NMP. In the case of dimethylamine, the amine was slowly bubbled into the solvent containing 2. The reaction mixture was

(1) Cameron, D. W.; Scott, P. M.; Todd, A. R. *J. Chem. Soc.* **1964**, 42.
(2) Brown, B. R.; Todd, A. R. *J. Chem. Soc.* **1954**, 1280.

0022-3263/88/1953-5959$01.50/0

Table I. Molar Ratios of Monoamine Adducts vs 3

	ratio		ratio
4a:3	76:24	**4e:3**	81:19
4b:3	81:19	**4f:3**	90:10
4c:3	62:38	**4g:3**	77:23
4d:3	35:65	**4h:3**	22:78

stirred at room temperature until the solution became homogeneous, usually for 3–4 days. The reaction mixture was poured into 400 mL of water and extracted with ether. The ether layer was separated and washed with a 10% HCl aqueous solution. After separation of the aqueous from the ether layer, the hydrochloride salt of **4a–g** (1:1) gradually precipitated out from the aqueous solution. The crude salt was collected by filtration and dried in a vacuum oven overnight. The dry salt was then suspended in chloroform and extracted with a saturated aqueous sodium bicarbonate solution. The chloroform layer was separated, dried ($MgSO_4$), and concentrated in vacuo to give the free amine adduct **4a–g**. The diol **3** was isolated after drying ($MgSO_4$) and concentration of the ether layer in vacuo.

4a·HCl: mp 165–172 °C. **4a**: 51% yield; mp 120–122 °C (ethanol–water); IR (KBr) 3420, 1605, 1470, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 9 H), 2.3 (s, 6 H), 3.6 (s, 2 H), 6.9–7.2 (m, 4 H); exact mass calcd for $C_{18}H_{23}NO_2$ 285.1729, obsd 285.1725.

4b·HCl: mp 235–237 °C. **4b**: 46% yield; mp 144–146 °C (ethanol–water); IR (KBr) 3460, 2940, 1605, 1470, 1202, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5 (m, 6 H), 2.2 (s, 9 H), 2.5 (m, 4 H), 3.6 (s, 2 H), 6.9–7.3 (m, 4 H); exact mass calcd for $C_{21}H_{27}NO_2$ 325.2042, obsd 325.2062.

4c·HCl: mp 205–207 °C. **4c**: 43% yield; mp 162–163 °C (ethanol–water); IR (KBr) 3410, 2920, 1605, 1470, 1200, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9 (m, 4 H), 2.3 (s, 9 H), 2.6 (m, 4 H), 3.8 (s, 2 H), 6.9–7.3 (m, 4 H), 7.5 (br s, 2 H); exact mass calcd for $C_{20}H_{25}NO_2$ 311.1885, obsd 311.1885.

4d·HCl: mp 233–235 °C. **4d**: 30% yield; mp 117–118 °C (ethanol–water); IR (KBr) 3440, 2920, 1605, 1478, 1230, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.3 (s, 9 H), 2.6 (m, 4 H), 3.7 (m, 6 H), 6.9–7.3 (m, 4 H); exact mass calcd for $C_{20}H_{25}NO_3$ 327.1834, obsd 327.1840.

4e·HCl: mp 175–178 °C. **4e**: 55% yield; mp 78–79 °C (purified through flash column chromatography using ether as the eluent); IR (KBr) 3400, 2930, 1600, 1470, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (m, 6 H), 1.0–1.8 (br m, 8 H), 2.1 (s, 3 H), 2.3 (s, 6 H), 2.5 (t, 4 H), 3.8 (s, 2 H), 6.9–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.0, 15.4, 16.0, 20.6, 28.4, 53.1, 58.3, 121.6, 123.3, 124.3, 124.9, 126.8, 128, 131.6, 133.5, 151.2, 155.3; exact mass calcd for $C_{24}H_{35}NO_2$ 369.2668, obsd 369.2661.

4f·HCl: mp 258 °C dec. **4f**: 66% yield; mp 56–58 °C (flash column chromatography, ethyl acetate–methanol, 10:1); IR (KBr) 3430, 2885, 1605, 1475, 1200, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 2.3 (s, 9 H), 3.95 (s, 2 H), 5.3 (br, 3 H), 7.0–7.3 (m, 4 H); exact mass calcd for $C_{20}H_{27}NO_2$ 313.2042, obsd 313.2053.

4g·HCl: mp 198–199 °C. **4g**: 45% yield; mp 98–99 °C (ethanol–water); IR (KBr) 3400, 2970, 1608, 1470, 1207, 1087 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, 6 H), 2.20 (s, 9 H), 2.54 (q, 4 H), 3.69 (s, 2 H), 6.89–7.20 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 15.8, 16.1, 46.2, 57.1, 121.3, 124.3, 125.0, 126.8, 128.0, 131.5, 133.5, 151.5, 155.5; exact mass calcd for $C_{20}H_{27}NO_2$ 313.2042, obsd 313.2046; UV ($CHCl_3$) 275 (ϵ 20 100), 247 nm (18 100).

Preparation of 4h. In a round-bottom flask, ϵ-caprolactam (11.31 g, 0.1 mol), **2** (5.0 g, 0.021 mol), and NMP (100 mL) were heated at 120 °C for 1 day. The reaction mixture was poured into water and then extracted with ether. The organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified through flash column chromatography using ether as the eluent. The first compound eluted was **3**, and the second one was **4h**: mp 224–225 °C; IR (KBr) 3440, 2930, 1610, 1590, 1480, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (br m, 6 H), 2.25 (s, 9 H), 2.50 (br m, 2 H), 3.45 (m, 2 H), 4.40 (s, 2 H), 7.1–7.2 (m, 4 H); exact mass calcd for $C_{22}H_{27}NO_3$ 353.1991, obsd 353.1987.

Acknowledgment. We thank Dorothy V. Temple for IR measurements, Paul E. Donahue, Joanne F. Smith, and Elizabeth A. Williams for ^{13}C NMR measurements, and Stephen B. Dorn for high-resolution mass spectra measurements.

A Simple Regiospecific Synthesis of Substituted Pyridines from 2-Aza 1,3-Dienes

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2-Aza 1,3-dienes have been used widely as synthons in the building of nitrogen six-membered rings, most of them through [4 + 2]-cycloaddition processes.[1] The ability of these systems to undergo reactions through their nitrogen atom is also well known. Thus, the formation of *N*-vinyl iminium salts[2] and the preparation of *N*-trimethylsilyldivinylamines[3] are processes described, in this context, in the literature.

In previous papers,[4] we have indicated the participation of unactivated 2-aza 1,3-dienes of the type **1** in Diels-Alder reactions with different heterodienophiles. Thus, for example, compounds **1** react with aldehydes **2** (X = O) by heating and/or in the presence of a Lewis acid to yield 1,3-oxazine derivatives **3**[4a] (see Scheme I). Surprisingly, when the reaction is carried out with aromatic aldehydes and trifluoroacetic acid, compounds identified as pentasubstituted pyridines were isolated as the only reaction products. The lack of general methods of synthesis of this type of pyridines[5,6] along with our own interest in the reactivity of 2-aza dienes **1** induced us to study this reaction more thoroughly.

In this paper, we report a new, simple, and regiospecific synthesis of substituted pyridines **4** by reacting 2-aza dienes **1** (R^1 = cyclohexyl, aryl; R^2 = alkyl) with aldehydes and aldimines **2** (X = O, NR^4) in the presence of catalytic amounts of trifluoroacetic acid. The reaction of 2-aza 1,3-dienes **1** (20 mmol), **2** (20 mmol), and trifluoroacetic acid (2 mmol) for 24 h in THF under reflux affords a crude residue, which consists exclusively of pentasubstituted pyridines **4**α or **4**β in high yields (see Scheme I and Table I).

The nature of the pyridine **4**α or **4**β (Scheme I) obtained is strongly dependent on the nature of X in **2**. Thus, symmetrical pyridines **4**α were the only products obtained when aldimines **2**[6] (X = NR^4) were used as starting material. The path to **4**α is most likely a direct condensation reaction between the aldimine and **1**, giving rise to the aza triene **5**. This can undergo an electrocyclic closure and loss of hydrogen to form **4**α.[7,8]

(1) (a) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. (b) Ghosez, L.; Serckx-Poncin, B.; Rivera, M.; Bayard Ph.; Sainte, F.; Demoulin, A.; Frisque-Hesbain, A.-M.; Mockel, A.; Muñoz, L.; Bernard-Henriet, Ch. J. *Heterocycl. Chem.* **1985**, *8*, 69. (c) Barluenga, J.; Tomás, M.; Ballesteros, A.; Gotor, V. *J. Chem. Soc., Chem. Commun.* **1987**, 1195.

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(6) For aldimines similar results were obtained when trifluoroacetic acid was substituted by a Lewis acid (e.g. BF_3·Et_2O) as the catalyst. For aldehydes see ref 4a.

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