3306 © *1991 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***64,*** *3306—3312 (1991)* [Vol. 64, No. 11

Neighboring Effect of a Carbonyl Group in Base-Induced Wittig-Type Rearrangements of Poly(4-nitrobenzyloxy)tropones to Bis- and Mono(α-hydroxy-4-nitrobenzyl)tropones

Bing Zhu YIN,[†] Akira MORI, and Hitoshi TAKESHITA*
Institute of Advanced Material Study, 86, Kyushu University,
Kasuga-koen, Kasuga, Fukuoka 816

(Received May 24, 1991)

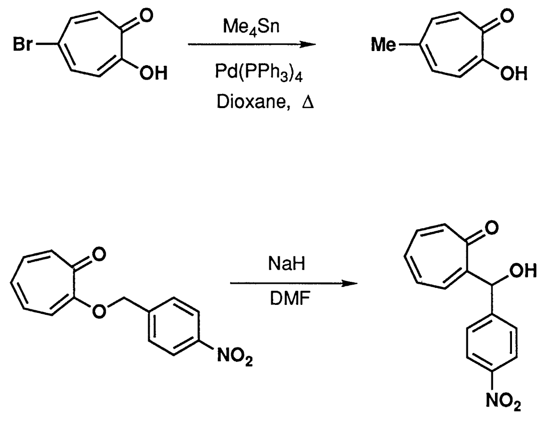
The base-catalyzed rearrangement of bis- and tris(4-nitrobenzyloxy)tropones gave (α-hydroxy-4-nitrobenzyl)tropones through a Wittig-type mechanism. Only the 4-nitrobenzyloxy group adjacent to the carbonyl group migrated. The carbonyl group played a role in facilitating the rearrangement by chelation with the sodium on the adjacent carbanion.

To overcome severe restrictions in introducing carbon substituents into the tropone ring,[1,2] several new approaches were recently elaborated: e.g., Banwell reported efficient palladium-mediated *ipso*-substitution processes of bromotropolones with various aryl-, alkenyl-, and alkyltrimethylstannanes.[3]

Recently, we exploited a new carbon–carbon bond formation in troponoids by means of base-catalyzed rearrangements of 2-(4-cyano-, 2-nitro-, and 4-nitrobenzyloxy)tropones and 2-(2-oxo-2-phenylethoxy)tropone to 2-[α-hydroxy-(4-cyano-, 2-nitro-, and 4-nitrobenzyl)]tropones and 2-(1-hydroxy-2-oxo-2-phenylethyl)tropone, respectively, via a Wittig-type mechanism.[4] This constituted a new regio-controlled introduction of carbon substituents into a tropone ring. In this paper, we describe an extention of this base-induced rearrangement to poly(benzyloxy)tropones to prepare poly(α-hydroxy-4-nitrobenzyl)tropones, in which only the benzyloxy group adjacent to the carbonyl group rearranged.

Results and Discussion

5-Hydroxytropolone dipotassium salt (**1**) and 4-nitrobenzyl bromide (**2**) in a hexamethylphosphoric triamide (HMPA) solution gave only a single product, 2,5-bis(4-nitrobenzyloxy)tropone (**3**). However, 3-hydroxytropolone dipotassium salt (**4**) and **2** gave three products (**5**—**7**); products **5** and **6** were identified to be 2,7-bis(4-nitrobenzyloxy)- and 2,3-bis(4-nitrobenzyloxy)tropones, respectively, from the NMR spectral data and **7** was identified as monobenzylated 3-(4-nitrobenzyloxy)tropolone. Along with these, an air-oxidized by-product **8**, which was no longer a troponoid derivative, was obtained. Its ^{1}H and ^{13}C NMR spectral data indicated it was bis(4-nitrobenzyl) (*Z*,*Z*)-2,4-hexadienedioate.



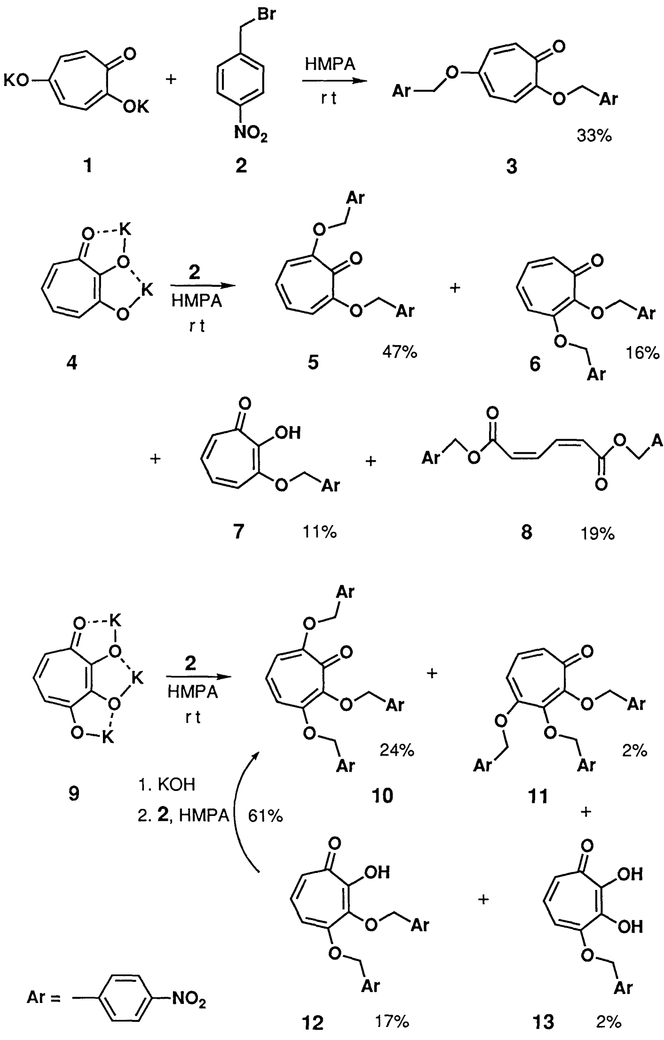
Scheme 1.

The reaction of 3,4-dihydroxytropolone tripotassium salt (**9**) with **2** gave four products (**10**—**13**): Two of them (**10** and **11**) were tris(4-nitrobenzyloxy)tropones; **10** had two singlets at a lower field (δ=5.37 and 5.40) than the other singlet at δ=5.12, whereas **11** had two singlets at a higher field (δ=5.09 and 5.16) than the other singlet at δ=5.29. Assuming that the chemical shift of benzylic methylene protons adjacent to the carbonyl group was lower, **10** was a 2,3,7-isomer, and **11** was a 2,3,4-isomer. With a similar series, chemical shifts of the methylene protons of **12** at δ=5.17 and 5.39 showed **12** to be 3,4-bis(4-nitrobenzyloxy)tropolone. The remaining isomer, **13**, was 3-hydroxy-4-(4-nitrobenzyloxy)tropolone.

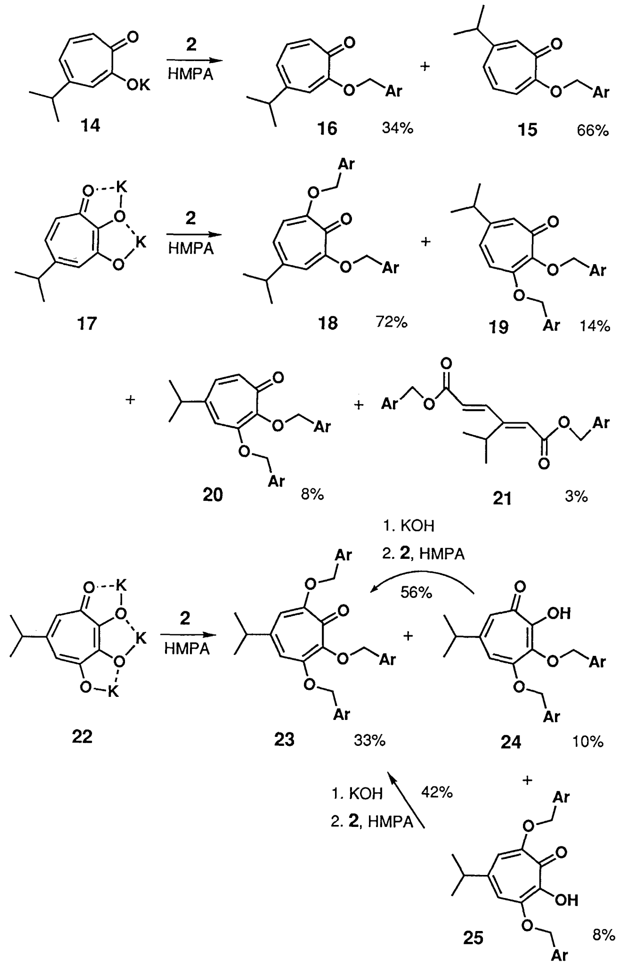
When 4-isopropyltropolone potassium salt (**14**) was allowed to react with **2**, two isomeric condensates, **15** and **16**, were isolated in 66 and 34% yields, respectively. The ^{1}H NMR spectrum of **15** showed a doublet signal at δ=6.67 (J=9.5 Hz), which was ascribable to the proton adjacent to the benzyloxy group. The magnitude of this vicinal coupling constant indicated that the two carbons bearing these protons had a single bond character. Therefore, **15** was 6-isopropyl-2-(4-nitrobenzyloxy)tropone and **16** was a 4-isopropyl-2-(4-nitrobenzyloxy) derivative.

From 3-hydroxy-5-isopropyltropolone dipotassium salt (**17**),[5] four products (**18**—**21**) were isolated in 72, 14, 8, and 3% yields, respectively. Three of them (**18**—**20**) were isomeric bis(4-nitrobenzyloxy)tropones. The coupling constant between H-5 and H-6 (J=10.2 Hz) of the main product **18** showed it to be 4-isopropyl-2,7-bis(4-nitrobenzyloxy)tropone. The structures of **19** and **20**

[†] On leave from Yanbian University, Yanji, Jilin, People's Republic of China.



Scheme 2.



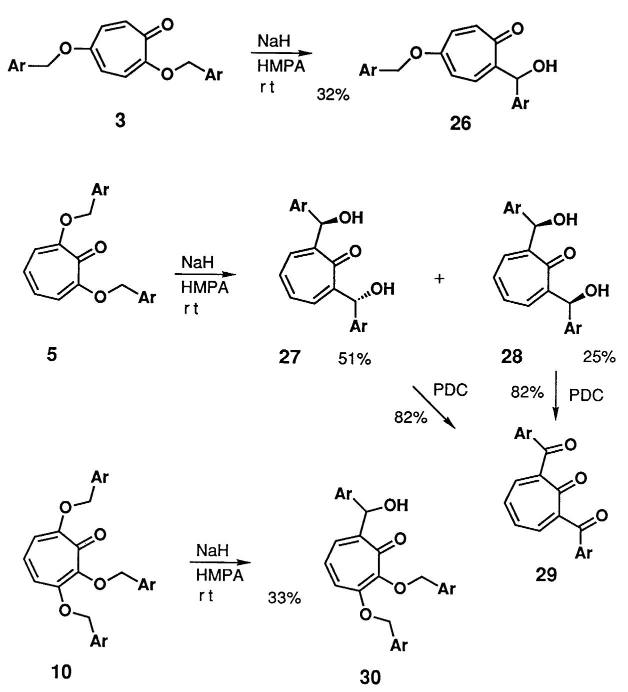
Scheme 3.

were deduced from the chemical shifts of seven-membered ring protons; **20** had a lower doublet at δ=7.21 (J=12.5 Hz) than that of **19** at δ=6.97 (J=12.0 Hz). Therefore, **19** was 6-isopropyl-2,3-bis(4-nitrobenzyloxy)-tropone and **20** was 5-isopropyl-2,3-bis(4-nitrobenzyloxy)tropone. The remaining **21** was an air-oxidized bis(4-nitrobenzyl) (*E*,*E*)-3-isopropyl-2,4-hexadienedioate.

The reaction of 3,4-dihydroxy-6-isopropyltropolone tripotassium salt (**22**) gave three products (**23**—**25**); two minor products **24** and **25** were bis(benzyloxy) derivatives and the latter was deduced to be 5-isopropyl-2,7-bis(4-nitrobenzyloxy)tropolone, whose NMR spectrum revealed an element of symmetry. Since the main product, **23**, was obtained by further reaction of **25**, it was 5-isopropyl-2,3,7-tri(4-nitrobenzyloxy)tropone. The remaining **24** is, therefore, assigned as 6-isopropyl-3,4-bis(4-nitrobenzyloxy)tropolone.

Base-Induced Rearrangements of Benzyloxytropones. When an HMPA solution of **3** was stirred in the presence of sodium hydride (NaH) at room temperature for 1 h, a single product, **26**, was obtained in 32% yield together with recovered **3** in 13% yield. The ^{1}H NMR spectrum of **26** in dimethyl-d_6 sulfoxide (DMSO-d_6) showed a singlet signal of two protons at δ=5.31 and a pair of doublet signals (J=4.4 Hz) at δ=5.92 and 6.23. One of the 4-nitrobenzyloxy groups migrated. The proton signals of the seven-membered ring of **3** appeared at δ=7.06 (d, J=11.0 Hz, H-2), which was assigned to H-2, and 6.63 (dd, J=11.0, 3.0 Hz, H-3) and those of **26** at δ=7.74 (d, J=10.3 Hz, H-2) and 6.81 (dd, J=10.3, 3.0 Hz, H-3). Therefore, **26** was 2-(α-hydroxy-4-nitrobenzyl)-5-(4-nitrobenzyloxy)tropone. Thus, the 4-nitrobenzyl group adjacent to the carbonyl group migrated exclusively.

On the other hand, a similar treatment of **5** afforded two products, **27** and **28**, in 51 and 25% yields, respectively. Pyridinium dichromate (PDC) oxidation of both **27** and **28** gave 2,7-bis(4-nitrobenzoyl)tropone (**29**). Therefore, **27** and **28** were stereoisomers. The stereochemistry of **27** and **28** was determined by liquid chromatography with a chiral stationary phase. Since the chromatogram of **27** was further separated into two peaks, **27** was a *dl*-mixture (R_f=12.2 and 16 min). On



Scheme 4.

the other hand, a meso isomer, **28**, remained as a single peak (R_f=13.3 min).

The base-induced reaction of **10** gave a single product, **30**. Its ^{1}H NMR spectrum in deuteriochloroform ($CDCl_3$) revealed two singlet signals due to benzylic methylene protons at δ=5.15 and 5.25 and a singlet single at δ=6.00, a benzylic methine proton. Therefore, two benzyloxy groups were intact. The low-field-shifted H-4 (7.47 from 7.22) and H-6 (7.56 from 7.06) of **30** indicated that the benzyloxy group at C-7 migrated.

Interestingly, the ^{1}H NMR spectrum of **30** in DMSO-d_6 showed a singlet signal of benzylic methylene protons at δ=5.37 and two pairs of AB quartets at δ=5.04 and 5.13 (J=12.8 Hz) and 6.10 and 6.34 (J=4.4 Hz). In $CDCl_3$, however, it showed three singlets at δ=5.15 (2H), 5.25 (2H), and 6.00 (1H). The latter of the AB quartets in DMSO-d_6 was assigned to be a benzylic methine proton signal and a hydroxyl proton signal. The appearance of the spin-coupling in DMSO-d_6 showed the formation of an intermolecular hydrogen bond involving the hydroxyl proton. On the other hand, the former of the quartets was assigned to be benzylic methylene protons; two benzylic protons are magnetically nonequivalent. The free rotation of the benzyloxy group at C-2 was hindered by the chelation between both carbonyl and hydroxyl groups and DMSO-d_6 as shown in **A** of Fig. 1.

Similarly, base-induced reactions of **15** and **16** gave the corresponding products **31** and **32**. From **18**, a diastereoisomeric mixture of **33** and **34** was obtained in 36 and 22% yields as observed with **5**. However, their chromatographic analyses with a chiral stationary phase were unsuccessful. Oxidations of **33** and **34** gave the same **35**.

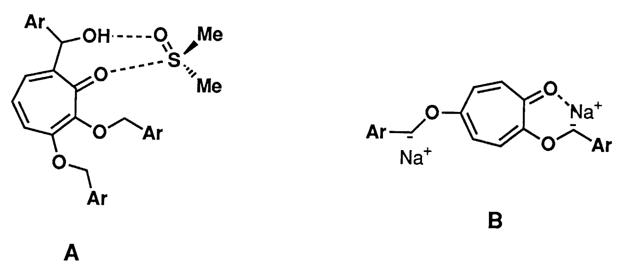
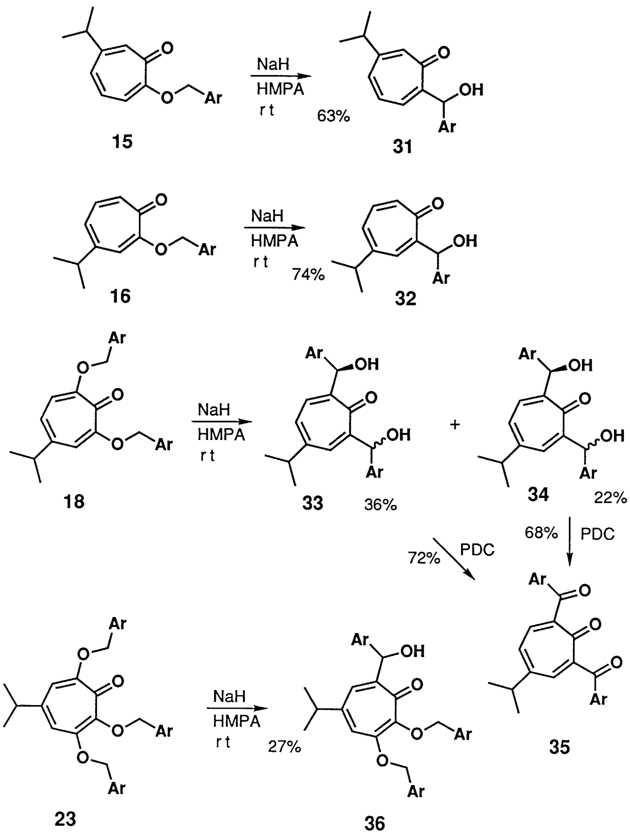


Fig. 1.



Scheme 5.

Finally, the reaction of **23** gave a single product, 5-isopropyl-7-(α-hydroxy-4-nitrobenzyl)-2,3-bis(4-nitrobenzyloxy)tropone (**36**).

A base-induced rearrangement of **3** gave only **26**. In 2,7-bis(4-nitrobenzyloxy)tropones, **5** and **18**, both benzyl groups migrated. Thus, the 4-nitrobenzyloxy group adjacent to the carbonyl group migrated exclusively. In tris(4-nitrobenzyloxy)tropones, **10** and **23**, only a 4-nitrobenzyloxy group at C-7 migrated. The inner benzyl group at C-2 was inactive due to the inhibition of an attack by NaH on methylene protons.

In conclusion, a Wittig-type rearrangement occurred exclusively at the benzyl group adjacent to the carbonyl group. The carbonyl group acted as an acceptor of the sodium cation to form an active naked carbanion at the neighboring position as shown in **B** of Fig. 1. Thus, the base-catalyzed rearrangement occurred at the *ipso*-position of bis- and tris(4-nitrobenzyloxy)tropones to give (α-hydroxy-4-nitrobenzyl)tropones. This method is currently being applied to prepare a 2,7-bis(functionalized)tropone derivative, which is a versatile starting material of functioned materials such as crown ethers with a tropone skeleton.

Experimental

Elemental analyses were performed by Mrs. M. Miyazawa of this Institute, Kyushu University. Melting points were measured with a Yanagimoto micro mp apparatus and were not corrected. NMR spectra were measured by JEOL FX 100 and GSX 270H spectrometers in $CDCl_3$, unless otherwise specified, and the chemical shifts were expressed in δ units. IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily materials using a JASCO IR-A 102 spectrometer. UV spectra were measured by the use of Hitachi U-3200 and U-3410 spectrophotometers. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane–ethyl acetate. HPLC was performed on a Chiralcel OJ column (Daicel Chemical Industries) by using a Waters M-45 pump and an S-301A UV detector (Soma Science) at 254 nm and by eluting with hexane–ethanol (1:2) with a flow rate of 3.5 cm^3 min^{-1}.

General Procedure of Condensation Reactions of Potassium Tropolonates (1, 4, 9, 14, 17, and 22) with 2. An EtOH solution (4 cm^3) of a tropolone derivative (1 mmol) and ca. two molar equivalents of KOH was stirred at room temperature for 1 h under a nitrogen atmosphere. After removing the solvent under reduced pressure, the residue was exhaustively dried under reduced pressure to give the potassium salt. An HMPA solution (6 cm^3) of the potassium salt and **2** (577 mg) was stirred at room temperature for 2 h. The mixture was diluted with water, acidified with 5% aqueous HCl solution (pH=4), and extracted with AcOEt. The organic layer was washed with water, dried with $MgSO_4$, and removed under reduced pressure. The residue was recrystallized and/or chromatographed on a silica-gel column (AcOEt–hexane=2:1 or $CHCl_3$) to give the product.

3: Yellow needles, mp 181—183 °C (AcOEt), 33% yield. ^1H NMR (DMSO-d_6) δ=5.28 (4H, s), 6.63 (1H, dd, *J*=11.0, 3.0 Hz), 7.06 (1H, d, *J*=11.0 Hz), 7.11 (1H, d, *J*=13.2 Hz), 7.31 (1H, dd, *J*=13.2, 3.0 Hz), 7.72 (2H, d, *J*=8.8 Hz), 7.73 (2H, d, *J*=8.8 Hz), and 8.27 (4H, d, *J*=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=68.5, 68.7, 109.4, 116.7, 123.5, (2C), 123.6 (2C), 128.2 (2C), 128.3 (2C), 132.6, 137.4, 143.8, 144.3, 147.0, 147.1, 157.7, 158.2, and 178.2; IR (KBr) 3076, 1630, 1581, 1514, 1348, 1248, 1194, 1126, 1007, 846, 824, and 735 cm^{-1}; UV ($CHCl_3$) 255 (ε 24700), 267 (23200 sh), 326 (15400), and 375 nm (5700 sh); MS *m*/*z* (%) 408 (M^+, 8), 273 (13), 137 (100), 106 (42), 90 (50), and 78 (67).

Found: C, 61.85; H, 4.24; N, 6.86%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.76; H, 3.95; N, 6.86%.

5: Colorless powder, mp 250—251 °C ($CHCl_3$), 47% yield. ^1H NMR (TFA-*d*) δ=5.83 (4H, s), 7.83 (4H, *J*=8.4 Hz), 8.39 (4H, d, *J*=8.4 Hz), and 8.3—8.5 (4H, m); ^{13}C NMR (TFA-*d*) δ=74.6 (2C), 118.7 (2C), 126.4 (4C), 130.9 (4C), 131.9 (2C), 141.5 (2C), 142.8 (2C), 150.3 (2C), and 161.6; IR (KBr) 3075, 1628, 1599, 1555, 1513, 1348, 1250, 1222, 1153, 1103, 1081, 1017, 855, 821, and 739 cm^{-1}; UV ($CHCl_3$) 248 (ε 39400), 271 (23100 sh), 324 (12850), 351 (10700), and 363 nm (8400 sh); MS *m*/*z* (%) 408 (M^+, 15), 272 (100), 257 (31), and 136 (44).

Found: C, 61.98; H, 4.27; N, 7.03%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.76; H, 3.95; N, 6.86%.

6: Pale yellow powder, mp 223—225 °C ($CHCl_3$), 16% yield. ^1H NMR (TFA-*d*) δ=5.62 (2H, s), 5.74 (2H, s), 7.51 (2H, d, *J*=8.5 Hz), 7.65 (2H, d, *J*=8.5 Hz), 8.13 (2H, d, *J*=8.5 Hz), 8.23 (2H, d, *J*=8.5 Hz), 8.40 (2H, br s), and 8.48 (2H, br s); ^{13}C NMR (TFA-*d*) δ=75.4, 78.0, 125.9 (2C), 126.3 (2C), 129.6 (2C), 131.5, 132.0 (2C), 138.1, 141.8, 144.9 (2C), 145.4, 149.6, 150.5, 154.7, 170.5, and 172.3; IR (KBr) 3074, 1630, 1606, 1555, 1513, 1476, 1348, 1249, 1224, 1153, 1080, 1017, and 855 cm^{-1}; UV ($CHCl_3$) 258 (ε 34000) and 326 nm (7800); MS *m*/*z* (%) 408 (M^+, 7), 272 (61), 257 (18), 136 (100), 106 (38), and 78 (26).

Found: C, 61.46; H, 4.07; N, 7.04%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.76; H, 3.95; N, 6.86%.

7: Yellow prisms, mp 165—166 °C (AcOEt–hexane), 11% yield. ^1H NMR δ=5.40 (2H, s), 7.00 (1H, dd, *J*=10.3, 9.9 Hz), 7.19 (1H, t, *J*=9.9 Hz), 7.24 (1H, d, *J*=10.3 Hz), 7.43 (1H, d, *J*=9.9 Hz), 7.67 (2H, d, *J*=8.8 Hz), and 8.26 (2H, d, *J*=8.8 Hz); ^{13}C NMR δ=70.3, 118.6, 122.6, 124.0 (2C), 126.2, 127.7 (2C), 131.5, 133.0, 147.8, 158.2, 163.3, and 170.9; IR (KBr) 3438, 3116, 1608, 1558, 1510, 1424, 1343, 1261, 1092, 1090, 848, 838, 757, and 735 cm^{-1}; UV ($CHCl_3$) 248 (ε 37700), 326 (8600), 364 (7800), and 374 nm (8200); MS *m*/*z* (%) 273 (M^+, 70), 137 (90), 122 (100), 90 (43), and 78 (38).

Found: *m*/*z* 273.0637 (M^+). Calcd for $C_{14}H_{11}NO_5$: M, 273.0636.

8: Colorless needles, mp 179—179.5 °C ($CHCl_3$), 19% yield. ^1H NMR (TFA-*d*) δ=5.48 (4H, s), 6.27 (2H, dd, *J*=8.8, 1.8 Hz), 7.67 (4H, d, *J*=8.8 Hz), 7.95 (2H, dd, *J*=8.8, 1.8 Hz), and 8.36 (4H, d, *J*=8.8 Hz); ^{13}C NMR (TFA-*d*) δ=68.3 (2C), 125.5 (2C), 126.1 (4C), 130.5 (4C), 141.1 (2C), 145.2 (2C), 149.6 (2C), and 170.3 (2C); IR (KBr) 3086, 1714, 1612, 1588, 1538, 1449, 1350, 1227, 1175, 1009, 845, 830, and 733 cm^{-1}; UV ($CHCl_3$) 273 nm (ε 45300); MS *m*/*z* (%) 412 (M^+, 7), 232 (59), 136 (100), 106 (30), and 78 (27).

Found: C, 58.23; H, 4.03; N, 6.80%. Calcd for $C_{20}H_{16}N_2O_8$: C, 58.25; H, 3.91; N, 6.79%.

10: Pale yellow needles, mp 188—190 °C ($CHCl_3$), 24% yield. ^1H NMR (DMSO-d_6) δ=5.12 (2H, s), 5.37 (2H, s), 5.40 (2H, s), 7.06 (1H, dm, *J*=9.6 Hz), 7.15 (1H, dd, *J*=11.4, 9.6 Hz), 7.22 (1H, dm, *J*=11.4 Hz), 7.66 (2H, d, *J*=8.8 Hz), 7.72 (2H, d, *J*=8.8 Hz), 7.77 (2H, d, *J*=8.8 Hz), 8.14 (2H, d, *J*=8.8 Hz), 8.20 (2H, d, *J*=8.8 Hz), and 8.30 (2H, d, *J*=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=68.9, 70.4, 71.4, 112.5, 119.5, 123.1 (2C), 123.4 (2C), 123.6 (2C), 128.2 (2C), 128.4 (4C), 128.8, 143.8, 144.0, 145.6, 146.8, 147.0, 147.1, 151.4, 158.6, 162.9, and 172.6; IR (KBr) 3075, 1605, 1581, 1547, 1521, 1349, 1233, 1070, 842, and 737 cm^{-1}; UV ($CHCl_3$) 265 (ε 60000), 333 (10800), and 353 nm (9300 sh); MS *m*/*z* (%) 559 (M^+, 0.3), 424 (29), 408 (27), 289 (46), 273 (51), 153 (54), 151 (53), 137 (100), 107 (32), and 77 (12).

Found: C, 60.05; H, 4.03; N, 7.40%. Calcd for $C_{28}H_{21}N_3O_{10}$: C, 60.11; H, 3.78; N, 7.51%.

11: Pale yellow needles, mp 185—187 °C ($CHCl_3$), 2% yield. ^1H NMR (DMSO-d_6) δ=5.09 (2H, s), 5.16 (2H, s), 5.29 (2H, s), 6.64 (1H, d, *J*=9.5 Hz), 6.97 (1H, d, *J*=11.8 Hz), 7.10 (1H, dd, *J*=11.8, 9.5 Hz), 7.43 (2H, d, *J*=8.8 Hz), 7.53 (2H, d,

J=8.8 Hz), 7.61 (2H, d, J=8.8 Hz), 8.08 (2H, d, J=8.8 Hz), 8.15 (2H, d, J=8.8 Hz), and 8.22 (2H, d, J=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=70.0, 72.4, 74.2, 108.4, 123.6 (4C), 124.0 (2C), 128.0 (2C), 128.1 (2C), 128.5, 128.7 (2C), 133.1, 133.3, 141.9, 143.6, 144.1, 147.7, 148.1, 152.4, 158.5, 158.7, and 180.6; IR (KBr) 3080, 1629, 1607, 1570, 1520, 1350, 1255, 1153, 1046, 850, 738, and 709 cm^{-1}; UV (CHCl$_3$) 263 (ε 53700) and 331 nm (11700); MS m/z (%) 559 (M$^+$, 0.7), 424 (50), 396 (26), 288 (64), 273 (34), 153 (22), and 137 (100).

Found: C, 60.07; H, 3.97; N, 7.46%. Calcd for $\mathrm{C_{28}H_{21}N_3O_{10}}$: C, 60.11; H, 3.78; N, 7.51%.

12: Yellow powder, mp 203—205 °C (AcOEt–hexane), 17% yield. ^{1}H NMR (DMSO-d_6) δ=5.17 (2H, s), 5.39 (2H, s), 7.08 (1H, d, J=11.4 Hz), 7.10 (1H, d, J=10.3 Hz), 7.35 (1H, dd, J=11.4, 10.3 Hz), 7.67 (2H, d, J=8.1 Hz), 7.70 (2H, d, J=8.1 Hz), 8.13 (2H, d, J=8.1 Hz), and 8.20 (2H, d, J=8.1 Hz); ^{13}C NMR (DMSO-d_6) δ=69.9, 72.0, 113.3, 117.5, 123.1 (2C), 123.4 (2C), 128.4 (2C), 128.6 (2C), 133.4, 143.6, 145.4, 146.8, 147.1 (2C), 160.6, 166.3, and 168.5; IR (KBr) 3450, 3150, 1607, 1583, 1519, 1467, 1345, 1263, 1160, 1046, 1007, and 737 cm^{-1}; UV (CHCl$_3$) 264 (ε 52000), 349 (7400), and 366 nm (6950); MS m/z (%) 424 (M$^+$, 8), 288 (32), 256 (6), 136 (100), 106 (31), 90 (33), and 78 (35).

Found: C, 59.29; H, 3.91; N, 6.64%. Calcd for $\mathrm{C_{21}H_{16}N_2O_8}$: C, 59.43; H, 3.80; N, 6.60%.

13: Colorless needles, mp 178—180 °C (CHCl$_3$), 2% yield. ^{1}H NMR (DMSO-d_6) δ=5.20 (2H, s), 6.88 (1H, d, J=11.4 Hz), 6.97 (1H, d, J=9.2 Hz), 7.13 (1H, dd, J=11.4, 9.2 Hz), 7.85 (2H, d, J=8.8 Hz), and 8.25 (2H, d, J=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=70.7, 112.2, 119.7, 123.1 (2C), 128.9 (2C), 132.0, 145.3, 145.5, 146.9, 160.4, 163.5, and 169.8; IR (KBr) 3290, 3120, 1603, 1576, 1516, 1470, 1423, 1346, 1290, 1214, 1155, 1056, 1008, and 737 cm^{-1}; UV (CHCl$_3$) 259 (ε 43400), 333 (6000), and 349 nm (5500); MS m/z (%) 289 (M$^+$, 42), 153 (10), 137 (100), and 90 (22).

Found: m/z 289.0586 (M$^+$). Calcd for $\mathrm{C_{14}H_{11}NO_6}$: M, 289.0586.

15: Colorless plates, mp 135—136 °C (AcOEt–hexane), 66% yield. ^{1}H NMR δ=1.24 (6H, d, J=7.0 Hz), 2.80 (1H, sept, J=7.0 Hz), 5.31 (2H, s), 6.67 (1H, d, J=9.5 Hz), 6.82 (1H, dd, J=11.0, 1.1 Hz), 6.93 (1H, dd, J=11.0, 9.5 Hz), 7.23 (1H, d, J=1.3 Hz), 7.64 (2H, d, J=8.8 Hz), and 8.24 (2H, d, J=8.8 Hz); ^{13}C NMR δ=23.0 (2C), 38.4, 69.4, 114.5, 124.0 (2C), 127.6 (2C), 130.6, 131.2, 135.1, 143.0, 147.7, 157.8, 163.1, and 180.2; IR (KBr) 3110, 2968, 1626, 1595, 1570, 1514, 1480, 1343, 1223, 1010, 902, 850, 787, 737, and 660 cm^{-1}; UV (CHCl$_3$) 242 (ε 30600), 270 (11900 sh), and 322 nm (9800); MS m/z (%) 299 (M$^+$, 61), 148 (100), 136 (15), 133 (17), 106 (20), 91 (23), and 78 (19).

Found: C, 68.51; H, 5.82; N, 4.42%. Calcd for $\mathrm{C_{17}H_{17}NO_4}$: C, 68.21; H, 5.73; N, 4.68%.

16: Colorless needles, mp 114—115 °C (AcOEt–hexane), 34% yield. ^{1}H NMR δ=1.16 (6H, d, J=7.0 Hz), 2.77 (1H, sept, J=7.0 Hz), 5.35 (2H, s), 6.73 (1H, br s), 6.81 (1H, dm, J=10.0 Hz), 7.1—7.2 (2H, m), 7.66 (2H, d, J=8.8 Hz), and 8.26 (2H, d, J=8.8 Hz); ^{13}C NMR δ=23.2 (2C), 38.8, 69.5, 117.8, 124.0 (2C), 126.0, 127.6 (2C), 136.0, 137.0, 143.3, 147.7, 153.7, 162.9, and 180.2; IR (KBr) 3110, 2960, 1596, 1546, 1521, 1493, 1344, 1258, 1219, 1179, 1148, 998, 827, and 737 cm^{-1}; UV (CHCl$_3$) 241 (ε 30300), 269 (11700 sh), and 327 nm (10300); MS m/z (%) 299 (M$^+$, 36), 148 (100), 136 (15), 133 (19), 106 (18), 91 (24), 89 (13), and 78 (19).

Found: C, 68.51; H, 5.71; N, 4.57%. Calcd for $\mathrm{C_{17}H_{17}NO_4}$: C, 68.21; H, 5.73; N, 4.68%.

18: Yellow needles, mp 154—155 °C, 72% yield. ^{1}H NMR (DMSO-d_6) δ=1.17 (6H, d, J=6.6 Hz), 2.87 (1H, sept, J=6.6 Hz), 5.32 (2H, s), 5.41 (2H, s), 6.87 (1H, dd, J=10.2, 1.1 Hz), 7.07 (1H, d, J=1.1 Hz), 7.17 (1H, d, J=10.2 Hz), 7.75 (2H, d, J=8.8 Hz), 7.79 (2H, d, J=8.8 Hz), 8.28 (2H, d, J=8.8 Hz), and 8.29 (2H, d, J=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=23.1 (2C), 37.2, 69.0, 79.1, 118.1, 118.4, 123.2, 123.5 (6C), 128.1, (4C), 144.5, 147.0, 147.3, 159.2, 160.2, and 172.3; IR (KBr) 2960, 1593, 1517, 1343, 1253, 1135, 1107, 840, and 735 cm^{-1}; UV (CHCl$_3$) 250 (ε 35300), 326 (10900), 353 (9900), and 366 nm (8000 sh); MS m/z (%) 450 (M$^+$, 14), 314 (59), 299 (32), 164 (12), 136 (100), 106 (31), 90 (23), and 78 (32).

Found: C, 63.80; H, 5.01; N, 6.08%. Calcd for $\mathrm{C_{24}H_{22}N_2O_7}$: C, 63.99; H, 4.92; N, 6.22%.

19: Yellow prisms, mp 127—128 °C, 14% yield. ^{1}H NMR (DMSO-d_6) δ=1.23 (6H, d, J=7.0 Hz), 2.75 (1H, sept, J=7.0 Hz), 5.22 (2H, s), 5.26 (2H, s), 6.83 (1H, dd, J=12.0, 1.8 Hz), 6.97 (1H, d, J=12.0 Hz), 7.13 (1H, d, J=1.8 Hz), 7.52 (2H, d, J=8.8 Hz), 7.63 (2H, d, J=8.7 Hz), 8.16 (2H, d, J=8.8 Hz), and 8.21 (2H, d, J=8.7 Hz); ^{13}C NMR (DMSO-d_6) δ=22.8 (2C), 37.8, 71.9, 72.7, 123.6 (2C), 123.9 (2C), 127.8 (2C), 128.5 (2C), 129.1, 132.1, 137.2, 137.4, 143.6, 144.6, 147.6, 147.8, 155.0, 156.5, and 181.0; IR (KBr) 2965, 1604, 1512, 1348, 1240, 1175, 1105, 849, and 737 cm^{-1}; UV (CHCl$_3$) 258 (ε 30150) and 327 nm (5400 sh); MS m/z (%) 450 (M$^+$, 12), 314 (60), 299 (29), 164 (13), 136 (100), 106 (31), 90 (26), and 78 (34).

Found: m/z 450.1417 (M$^+$). Calcd for $\mathrm{C_{24}H_{22}N_2O_7}$: M, 450.1426.

20: Pale yellow needles, mp 180—181 °C, 8% yield. ^{1}H NMR (DMSO-d_6) δ=1.21 (6H, d, J=7.0 Hz), 2.77 (1H, sept, J=7.0 Hz), 5.22 (2H, s), 5.26 (2H, s), 6.86 (1H, d, J=1.8 Hz), 7.06 (1H, dd, J=12.5, 1.8 Hz), 7.21 (1H, d, J=12.5 Hz), 7.53 (2H, d, J=8.8 Hz), 7.63 (2H, d, J=8.8 Hz); 8.16 (2H, d, J=8.8 Hz), and 8.21 (2H, d, J=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=22.9 (2C), 37.9, 72.0, 73.0, 123.6 (2C), 123.9 (2C), 126.2, 127.9 (2C), 128.6 (2C), 135.6, 140.4, 143.7, 144.6, 147.7, 147.8, 151.5, 154.4, 158.0, and 180.6; IR (KBr) 2957, 1624, 1601, 1553, 1349, 1264, 1235, 1140, 1086, 1000, 850, and 735 cm^{-1}; UV (CHCl$_3$) 257 (ε 33400) and 323 nm (10600); MS m/z (%) 450 (M$^+$, 9), 314 (54), 299 (17), 164 (17), 136 (100), 106 (37), 90 (34), and 78 (53).

Found: C, 63.68; H, 5.04; N, 6.01%. Calcd for $\mathrm{C_{24}H_{22}H_2O_7}$: C, 63.99; H, 4.92; N, 6.22%.

21: Colorless needles, mp 165—166 °C, 3% yield. ^{1}H NMR δ=1.18 (6H, d, J=6.6 Hz), 2.85 (1H, sept, J=6.6 Hz), 5.28 (2H, s), 5.33 (2H, s), 6.02 (1H, s), 6.29 (1H, d, J=16.5 Hz), 7.56 (2H, d, J=8.8 Hz), 7.57 (2H, d, J=8.8 Hz), 8.23 (2H, d, J=8.8 Hz), 8.24 (2H, d, J=8.8 Hz), and 8.66 (1H, d, J=16.5 Hz); ^{13}C NMR δ=20.2 (2C), 30.8, 64.9, 65.0, 119.1, 122.3, 123.9 (5C), 128.4 (2C), 128.6 (2C), 141.2, 143.0, 143.2, 147.8, 159.2, 165.3, and 166.0; IR (KBr) 2974, 1727, 1598, 1518, 1346, 1276, 1235, 1169, 1138, 1016, 860, 833, and 735 cm^{-1}; UV (CHCl$_3$) 273 nm (ε 39100); MS m/z (%) 454 (M$^+$, 5), 274 (100), 136 (83), 106 (25), 90 (15), and 78 (21).

Found: C, 60.59; H, 5.15; N, 6.08%. Calcd for $\mathrm{C_{23}H_{22}N_2O_8}$: C, 60.79; H, 4.88; N, 6.17%

23: Pale yellow crystals, mp 93—95 °C, 33% yield. ^{1}H NMR δ=1.17 (6H, d, J=6.0 Hz), 2.78 (1H, br s), 5.22 (2H, s), 5.25 (2H, s), 5.33 (2H, s), 6.70 (1H, br s), 6.78 (1H, br s), 7.54 (2H, d, J=8.8 Hz), 7.69 (4H, d, J=8.8 Hz), 8.17 (2H, d, J=8.8 Hz), 8.21 (2H, d, J=8.8 Hz), and 8.27 (2H, d, J=8.8 Hz);

^{13}C NMR δ=23.3 (2C), 31.6, 70.0, 72.4, 72.5, 115.7, 119.7, 123.5, (2C), 123.9 (3C), 124.0 (2C), 127.7 (2C), 127.9 (2C), 128.7 (2C), 143.0, 143.5, 144.8, 147.6, 147.8, 149.5, 152.2, 159.0, 162.4, and 173.8; IR (KBr) 3082, 2964, 1601, 1573, 1519, 1345, 1243, 1194, 1067, 1013, 850, and 737 cm^{-1}; UV (CHCl$_3$) 264 (ε 58100) and 334 nm (11100); MS *m*/*z* (%) 601 (M$^+$, 0.5), 466 (59), 450 (55), 330 (47), 315 (100), 303 (47), 180 (61), 167 (82), 153 (55), 151 (67), 137 (76), 107 (37), and 77 (23).

Found: C, 61.76; H, 4.65; N, 6.89%. Calcd for $C_{31}H_{27}N_3O_{10}$: C, 61.89; H, 4.52; N, 6.99%.

24: Yellow needles, mp 169—170 °C (AcOEt–hexane), 10% yield. ^{1}H NMR δ=1.20 (6H, d, *J*=7.0 Hz), 2.79 (1H, sept, *J*=7.0 Hz), 4.27 (1H, br s), 5.31 (2H, s), 5.36 (2H, s), 6.64 (1H, s), 6.93 (1H, s), 7.68 (4H, d, *J*=8.8 Hz), 8.22 (2H, d, *J*=8.8 Hz), and 8.26 (2H, d, *J*=8.8 Hz); ^{13}C NMR δ=23.1 (2C), 38.9, 69.9, 71.8, 114.7, 119.2, 123.7, 123.8 (2C), 124.0 (2C), 127.7 (2C), 129.1 (2C), 143.0, 143.9, 145.5, 147.8, 147.9, 150.7, 158.6, and 161.6; IR (KBr) 2964, 1605, 1520, 1345, 1234, 1199, 1047, 848, 822, and 738 cm^{-1}; UV (CHCl$_3$) 263 (ε 53700) and 328 nm (9800); MS *m*/*z* (%) 466 (M$^+$, 12), 422 (20), 330 (21), 303 (56), 167 (100), and 136 (22).

Found: C, 61.93; H, 4.95; N, 5.87%. Calcd for $C_{24}H_{22}N_2O_8$: C, 61.80; H, 4.75; N, 6.01%.

25: Yellow prisms, mp 180—182 °C, 8% yield. ^{1}H NMR δ=1.16 (6H, d, *J*=7.0 Hz), 2.81 (1H, sept, *J*=7.0 Hz), 5.39 (4H, s), 7.01 (2H, s), 7.68 (4H, d, *J*=8.8 Hz), and 8.26 (4H, d, *J*=8.8 Hz); ^{13}C NMR δ=23.8, 39.1, 71.0 (2C), 121.4 (2C), 123.9 (4C), 127.9 (4C), 143.6 (2C), 145.2 (2C), 147.8 (2C), 154.5 (2C), and 161.4 (2C); IR (KBr) 3100, 2966, 1604, 1542, 1518, 1469, 1402, 1344, 1226, 1094, 844, and 737 cm^{-1}; UV (CHCl$_3$) 264 (ε 51300), 330 (8400), 359 (8300), and 374 nm (8200); MS *m*/*z* (%) 466 (M$^+$, 22), 330 (34), 315 (51), 180 (26), 136 (100), 106 (41), 90 (43), and 78 (49).

Found: C, 61.76; H, 4.65; N, 5.93%. Calcd for $C_{24}H_{22}N_2O_8$: C, 61.80; H, 4.75; N, 6.01%.

Reactions of 12, 25, and 24 with 2. Under conditions similar to those described above, the reactions of **12**, **25**, and **24** with **2** gave **10** (61% yield), **23** (42% yield), and **23** (56% yield), respectively.

Base-Induced Rearrangement of 4-Nitrobenzyl Ethers. A Typical Example. An HMPA solution (3.5 cm^3) of NaH (3.5 mg) and **3** (59 mg) was stirred at room temperature for 1 h. The mixture was diluted with water, acidified with 5% aqueous HCl solution (pH=3), and extracted with AcOEt. The extract was dried with MgSO$_4$ and chromatographed on a silica-gel column (AcOEt:hexane=1:1) to give 19 mg (32% yield) of **26** and 7.5 mg (13% yield) of recovered **3**.

26: Yellow powder, mp 156—158 °C. ^{1}H NMR (DMSO-*d*$_6$) δ=5.31 (2H, s), 5.92 (1H, d, *J*=4.4 Hz), 6.23 (1H, d, *J*=4.4 Hz), 6.81 (1H, dd, *J*=10.3, 3.0 Hz), 6.99 (1H, d, *J*=13.2 Hz), 7.25 (1H, dd, *J*=13.2, 3.0 Hz), 7.64 (2H, d, *J*=8.8 Hz), 7.74 (2H, d, *J*=8.8 Hz), 7.74 (1H, d, *J*=10.3 Hz), 8.15 (2H, d, *J*=8.8 Hz), and 8.28 (2H, d, *J*=8.8 Hz); ^{13}C NMR (DMSO-*d*$_6$) δ=68.6, 69.0, 110.1, 123.1 (2C), 123.6 (2C), 127.5 (2C), 128.5 (2C), 133.2, 134.0, 140.8, 143.3, 146.3, 147.2 (2C), 152.0, 161.0, and 183.2; IR (KBr) 3432, 1606, 1521, 1454, 1348, 1256, 1217, 1195, 859, and 736 cm^{-1}; UV (CHCl$_3$) 266 (ε 21500) and 326 nm (16100); MS *m*/*z* (%) 408 (M$^+$, 21), 272 (83), 244 (56), 136 (100), 106 (50), and 78 (46).

Found: C, 61.94; H, 4.16; N, 6.81%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.76; H, 3.95; N, 6.86%.

27: Yellow prisms, mp 201—203 °C (AcOEt–hexane), 51% yield. ^{1}H NMR (DMSO-*d*$_6$) δ=5.94 (2H, d, *J*=4.4 Hz), 6.24 (2H, d, *J*=4.4 Hz), 7.3—7.4 (2H, m), 7.63 (4H, d, *J*=8.8 Hz), 7.9—8.0 (2H, m), and 8.15 (4H, d, *J*=8.8 Hz); ^{13}C NMR (DMSO-*d*$_6$) δ=70.0 (2C), 123.1 (4C), 127.9 (4C), 133.7 (2C), 133.8 (2C), 146.4 (2C), 151.2 (2C), 154.2 (2C), and 182.7; IR (KBr) 3415, 1597, 1519, 1343, 1107, 1074, 1036, and 740 cm^{-1}; UV (CHCl$_3$) 272 (ε 24500) and 322 nm (12000); MS *m*/*z* (%) 408 (M$^+$, 1), 406 (7), 390 (100), 315 (9), 150 (34), and 77 (18).

Found: C, 61.81; H, 4.14; N, 6.81%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.76; H, 3.95; N, 6.86%.

28: Yellow prisms, mp 231—232 °C (CHCl$_3$), 25% yield. ^{1}H NMR (DMSO-*d*$_6$) δ=5.97 (2H, s), 6.31 (2H, br s), 7.3—7.35 (2H, m), 7.43 (4H, d, *J*=8.8 Hz), 7.85—7.9 (2H, m), and 7.97 (4H, d, *J*=8.8 Hz); ^{13}C NMR (DMSO-*d*$_6$) δ=69.8 (2C), 122.8 (4C), 127.7 (4C), 132.8 (2C), 133.5 (2C), 146.1 (2C), 151.0 (2C), 153.5 (2C), and 183.4; IR (KBr) 3280, 1599, 1564, 1515, 1345, 1109, 1059, 859, 835, and 710 cm^{-1}; UV (CHCl$_3$) 273 (ε 23800) and 322 nm (11450); MS *m*/*z* (%) 408 (M$^+$, 1), 406 (8), 390 (100), 315 (15), 165 (31), 150 (39), 104 (26), and 77 (26).

Found: C, 61.83; H, 4.07; N, 6.70%. Calcd for $C_{21}H_{16}N_2O_7$: C, 61.76; H, 3.95; N, 6.86%.

30: Yellow powder, mp 185—187 °C (AcOEt–hexane), 33% yield. ^{1}H NMR δ=5.15 (2H, s), 5.25 (2H, s), 6.00 (1H, s), 7.06 (1H, dd, *J*=12.0, 8.9 Hz), 7.16 (1H, dm, *J*=12.0 Hz), 7.47 (1H, dm, *J*=8.9 Hz), 7.51 (2H, d, *J*=8.8 Hz), 7.53 (2H, d, *J*=8.8 Hz), 7.63 (2H, d, *J*=8.8 Hz), 8.13 (2H, d, *J*=8.8 Hz), 8.18 (2H, d, *J*=8.8 Hz), and 8.20 (2H, d, *J*=8.8 Hz); ^{1}H NMR (DMSO-*d*$_6$) δ=5.04 (1H, d, *J*=12.8 Hz), 5.13 (1H, d, *J*=12.8 Hz), 5.37 (2H, s), 6.10 (1H, d, *J*=4.4 Hz), 6.34 (1H, d, *J*=4.4 Hz), 7.29 (1H, dd, *J*=11.7, 9.2 Hz), 7.47 (1H, d, *J*=11.7 Hz), 7.59 (1H, d, *J*=9.2 Hz), 7.63 (2H, d, *J*=8.8 Hz), 7.67 (2H, d, *J*=8.8 Hz), 7.84 (1H, d, *J*=8.8 Hz), 8.09 (2H, d, *J*=8.8 Hz), 8.16 (2H, d, *J*=8.8 Hz), and 8.19 (2H, d, *J*=8.8 Hz); ^{13}C NMR δ=72.2, 72.5, 75.5, 123.6 (4C), 123.7, 124.0 (3C), 127.1 (2C), 127.8 (2C), 128.4 (2C), 129.1, 129.7, 133.4, 143.0, 144.1, 147.4, 149.3, 151.4, 155.1, 158.3, and 180.1; ^{13}C NMR (DMSO-*d*$_6$) δ=69.8, 70.7, 71.2, 123.1 (4C), 123.4 (2C), 126.7, 126.9, 127.9 (2C), 128.3 (2C), 128.4 (2C), 129.8, 131.0, 144.0, 145.2, 146.7, 147.0, 151.5, 153.2, 157.6, and 177.9; IR (KBr) 3438, 1606, 1512, 1348, 1254, 1167, 853, 821, and 710 cm^{-1}; UV (CHCl$_3$) 265 (ε 48800), 329 (9800), and 357 nm (7000 sh); MS *m*/*z* (%) 559 (M$^+$, 0.5), 422 (43), 408 (24), 237 (23), 151 (100), 137 (87), 121 (26), and 107 (23)

Found: C, 60.28; H, 3.96; N, 7.62%. Calcd for $C_{28}H_{21}N_3O_{10}$: C, 60.11; H, 3.78; N, 7.51%.

31: A pale yellow oil, 63% yield. ^{1}H NMR δ=1.24 (6H, d, *J*=7.0 Hz), 2.85 (1H, sept, *J*=7.0 Hz), 3.99 (1H, br s), 5.90 (1H, s), 6.97 (1H, dd, *J*=11.7, 1.1 Hz), 6.98 (1H, dd, *J*=9.1, 1.1 Hz), 7.10 (1H, dd, *J*=11.7, 9.1 Hz), 7.47 (1H, d, *J*=1.1 Hz), 7.62 (2H, d, *J*=8.8 Hz), and 8.17 (2H, d, *J*=8.8 Hz); ^{13}C NMR δ=23.0, 23.1, 38.4, 76.0, 123.5 (2C), 127.2 (2C), 131.0, 137.6, 137.9, 139.6, 147.2, 149.6, 151.9, 155.8, and 186.6; IR (NaCl) 3367, 2977, 1628, 1598, 1520, 1346, 1108, and 860 cm^{-1}; UV (MeOH) 215 (ε 20600), 235 (20800), 277 (12200), 305 (10500), and 320 nm (9900); MS *m*/*z* (%) 299 (M$^+$, 100), 149 (93), 105 (17), 77 (23), and 43 (20).

Found: C, 68.50; H, 5.76; N, 4.74%. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68%.

32: A pale yellow oil, 74% yield. ^{1}H NMR δ=1.22 (6H, d, *J*=7.0 Hz), 2.78 (1H, sept, *J*=7.0 Hz), 3.60 (1H, br s), 5.84 (1H, s), 7.0—7.1 (3H, m), 7.37 (1H, m), 7.62 (2H, d, *J*=8.8 Hz), and 8.17 (2H, d, *J*=8.8 Hz); ^{13}C NMR δ=22.7, 22.8, 38.2, 75.2, 123.5

(2C), 127.2 (2C), 132.9, 135.4, 137.1, 138.7, 147.3, 149.4, 152.2, 158.0, and 186.9; IR (NaCl) 3375, 3027, 1628, 1606, 1552, 1526, 1348, 1090, and 842 cm^{-1}; UV (MeOH) 216 (ε 20800), 237 (20800), 276 (15700), and 316 nm (8300 sh); MS m/z (%) 299 (M$^+$, 100), 256 (55), 149 (23), and 77 (13).

Found: m/z 299.1157 (M$^+$). Calcd for $C_{17}H_{17}NO_4$: M, 299.1157.

33: Yellow crystals, mp 219—221 °C, 36% yield. ^{1}H NMR (DMSO-d_6) δ=1.23 (6H, d, J=7.0 Hz), 2.94 (1H, sept, J=7.0 Hz), 5.92 (1H, d, J=2.2 Hz), 5.96 (1H, d, J=2.2 Hz), 6.18 (1H, d, J=4.1 Hz), 6.28 (1H, d, J=4.1 Hz), 7.24 (1H, dd, J=9.5, 1.4 Hz), 7.63 (2H, d, J=8.8 Hz), 7.64 (2H, d, J=8.8 Hz), 7.85 (1H, d, J=9.5 Hz), 7.92 (1H, d, J=1.4 Hz), 8.14 (2H, d, J=8.8 Hz), and 8.15 (2H, d, J=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=22.8, 22.9, 37.4, 69.5, 70.2, 123.1 (4C), 127.7 (2C), 127.9 (2C), 129.5, 134.0, 134.6, 146.3, 146.4, 151.3, 151.5, 151.9, 153.4, 154.1, and 182.1; IR (KBr) 3495, 2960, 1594, 1552, 1515, 1342, 1074, 852, 831, and 703 cm^{-1}; UV (CHCl$_3$) 272 (ε 24200) and 324 nm (14000 sh); MS m/z (%) 450 (M$^+$, 1), 448 (9), 432 (100), 357 (11), 165 (12), 150 (35), 120 (11), 104 (26), 77 (14), and 76 (11).

Found: C, 63.91; H, 5.12; N, 6.20%. Calcd for $C_{24}H_{22}N_2O_7$: C, 63.99; H, 4.92; N, 6.22%.

34: Yellow crystals, mp 205—207 °C, 22% yield. ^{1}H NMR (DMSO-d_6) δ=1.22 (6H, d, J=7.0 Hz), 2.92 (1H, sept, J=7.0 Hz), 5.96 (1H, d, J=4.5 Hz), 5.98 (1H, d, J=4.5 Hz), 6.25 (1H, d, J=4.4 Hz), 6.34 (1H, d, J=4.4 Hz), 7.20 (1H, dd, J=9.5, 1.4 Hz), 7.43 (2H, d, J=8.8 Hz), 7.46 (2H, d, J=8.8 Hz), 7.78 (1H, d, J=9.5 Hz), 7.85 (1H, d, J=1.4 Hz), 7.97 (2H, d, J=8.8 Hz), and 7.98 (2H, d, J=8.8 Hz); ^{13}C NMR (DMSO-d_6) δ=22.8, 22.9, 37.3, 69.5, 70.1, 79.1, 122.8 (3C), 127.5 (2C), 127.6, 127.7 (2C), 129.2, 133.2, 133.8, 146.1 (2C), 151.1, 151.2, 151.3, 153.7, and 182.8; IR (KBr) 3485, 2965, 1598, 1519, 1344, 1080, 856, 832, and 707 cm^{-1}; UV (CHCl$_3$) 242 (ε 23200), 272 (23100), and 325 nm (12700 sh); MS m/z (%) 450 (M$^+$, 4), 448 (41), 432 (100), 298 (36), 150 (66), 120 (20), 104 (38), 77 (19), and 76 (19).

Found: C, 64.22; H, 5.21; N, 6.23%. Calcd for $C_{24}H_{22}N_2O_7$: C, 63.99; H, 4.92; N, 6.22%.

36: A yellow oil, 27% yield. ^{1}H NMR δ=1.24 (6H, d, J=6.4 Hz), 2.86 (1H, sept, J=6.4 Hz), 5.10 (2H, s), 5.24 (2H, s), 5.98 (1H, s), 7.00 (1H, br s), 7.44 (1H, br s), 7.53 (4H, d, J=8.0 Hz), 7.62 (2H, d, J=8.0 Hz), 8.11 (2H, d, J=8.0 Hz), 8.17 (2H, d, J=8.0 Hz), and 8.21 (2H, d, J=8.0 Hz); ^{1}H NMR (DMSO-d_6) δ=1.23 (6H, d, J=6.6 Hz), 2.98 (1H, sept, J=6.6 Hz), 5.00 (1H, d, J=11.8 Hz), 5.08 (1H, d, J=11.8 Hz), 5.39 (2H, s), 6.10 (1H, s), 6.38 (1H, br s), 7.23 (1H, s), 7.59 (2H, d, J=8.8 Hz), 7.64 (2H, d, J=8.8 Hz), 7.73 (2H, d, J=8.8 Hz), 7.81 (1H, s), 8.09 (2H, d, J=8.8 Hz), 8.16 (2H, d, J=8.8 Hz), and 8.19 (2H, d, J=8.8 Hz); ^{13}C NMR δ=23.1, 23.2, 38.6, 72.2, 72.7, 76.3, 123.6 (4C), 123.7, 123.9 (2C), 125.6, 127.0, 127.2 (2C), 127.8 (2C), 128.4 (2C), 135.3, 143.2, 144.2, 147.3, 149.5, 150.5, 151.0, 153.7, 158.7, and 179.8; ^{13}C NMR (DMSO-d_6) δ=23.1, 23.2, 38.6, 72.2, 72.7, 76.3, 123.6 (4C), 123.7, 123.9 (2C), 125.6, 127.0, 127.2 (2C), 127.8 (2C), 128.4 (2C), 135.3, 143.2, 144.2, 147.3, 149.5, 150.5, 151.0, 153.7, 158.7, and 179.8; IR (NaCl) 3380, 2962, 1605, 1522, 1348, 1260, 1167, 1110, 1013, 853, and 739 cm^{-1}; UV (CHCl$_3$) 265 (ε 39700) and 329 nm (8900); MS m/z (%) 601 (M$^+$, 1), 583 (2), 464 (100), 450 (93), 330 (78), 315 (45), 151 (62), and 137 (63).

Found: C, 62.12; H, 4.68; N, 7.10%. Calcd for $C_{31}H_{27}N_3O_{10}$: C, 61.89; H, 4.52; N, 6.99%.

PDC-Oxidation. A Typical Example. A CH_2Cl_2 solution (20 cm^3) of **27** (39 mg), PDC (180 mg), and celite (600 mg) was stirred at room temperature for 16 h. The mixture was chromatographed on a silica-gel column (AcOEt:hexane=1:1) to give 31.7 mg (82% yield) of **29**.

29: Pale yellow needles, mp 261—265 °C (decomp). ^{1}H NMR (DMSO-d_6) δ=7.55—7.6 (2H, m), 7.8—7.85 (2H, m), 8.05 (4H, d, J=9.2 Hz), and 8.29 (4H, d, J=9.2 Hz); ^{13}C NMR (DMSO-d_6) δ=123.9 (4C), 129.9 (4C), 137.2 (2C), 137.9 (2C), 140.1 (2C), 150.0 (2C), 150.7 (2C), 183.8, and 194.4 (2C); IR (KBr) 3108, 1683, 1602, 1561, 1521, 1353, 1271, 1241, 885, 850, and 749 cm^{-1}; UV (CHCl$_3$) 270 (ε 30700) 312 (11100 sh), and 343 nm (6600); MS m/z (%) 404 (M$^+$, 100), 376 (32), 359 (34), 329 (53), 254 (37), 226 (31), 150 (63), 104 (64), and 76 (53).

Found: C, 62.37; H, 3.11; N, 6.78%. Calcd for $C_{21}H_{12}N_2O_7$: C, 62.38; H, 2.99; N, 6.93%.

35: Pale yellow needles, mp 193—195 °C (AcOEt–hexane), 72% yield. ^{1}H NMR δ=1.33 (6H, d, J=7.0 Hz), 2.97 (1H, sept, J=7.0 Hz), 7.22 (1H, dd, J=9.2, 1.8 Hz), 7.46 (1H, d, J=1.8 Hz), 7.56 (1H, d, J=9.2 Hz), 7.95 (2H, d, J=8.8 Hz), 7.97 (2H, d, J=8.8 Hz), 8.26 (2H, d, J=8.8 Hz), and 8.27 (2H, d, J=8.8 Hz); ^{13}C NMR δ=22.8 (2C), 38.5, 123.9 (4C), 130.0 (2C), 130.1 (2C), 131.4, 137.9, 138.3, 140.5, 140.7, 148.7, 150.4, 150.5, 150.9, 158.7, 183.6, and 194.2 (2C); IR (KBr) 3110, 2975, 1679, 1602, 1557, 1518, 1347, 1256, and 845 cm^{-1}; UV (CHCl$_3$) 265 (ε 35800) and 316 nm (13600); MS m/z (%) 446 (M$^+$, 95), 418 (66), 296 (100), 150 (84), 104 (87), and 76 (53).

Found: C, 64.77; H, 4.20; N, 6.54%. Calcd for $C_{24}H_{18}N_2O_7$: C, 64.57; H, 4.06; N, 6.28%.

References

1) T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Jpn. Acad.*, **27**, 419 (1951); W. von E. Doering and C. F. Haskey, *J. Am. Chem. Soc.*, **74**, 5688 (1952); T. Nozoe, T. Mukai, J. Minegishi, and T. Fujisawa, *Sci. Rep. Tohoku Univ., Ser. I*, **37**, 388 (1953); T. Mukai, *Bull. Chem. Soc. Jpn.*, **31**, 852 (1958).

2) T. Nozoe, K. Takase, and H. Matsumura, "Non-Benzenoid Aromatic Compounds, Vol. 13 of Dai Yuki Kagaku (Comprehensive Organic Chemistry), " ed by M. Kotake, Asakura Shoten, Tokyo (1960), pp. 119—133.

3) M. G. Banwell, *Aust. J. Chem.*, **44**, 1 (1991), and references cited therein.

4) H. Takeshita, A. Mori, and H. Suizu, *Bull. Chem. Soc. Jpn.*, **60**, 1429 (1987); H. Takeshita, A. Mori, and H. Suizu, *Chem. Lett.*, **1986**, 593.