22.9, 22.7, 13.9, 13.8; MS (NaCl added, m/z) 322 (MNa^+, 13), 300 (MH^+, 60), 282 (11), 160 (83), 143 (100), 141 (86), 125 (78), 114 (29). One diastereomer was separated by flash chromatography (silica gel, 230-400 mesh, EtOAc-hexane, eluent gradient of 1:4 to 1:1): mp 159.0-159.5 °C; ^1H NMR ($(CD_3)_2CO$) δ 7.84-7.86 (m, 2 H), 7.53-7.63 (m, 3 H), 6.70 (d, J = 9.2, 1 H), 4.43 (d, J = 4.1, 1 H), 3.93 (s, 1 H), 3.83-3.89 (m, 2 H), 1.65-1.70 (m, 2 H), 1.47-1.62 (m, 1 H), 1.36-1.38 (m, 2 H), 1.20-1.26 (m, 3 H), 0.83 (t, J = 7.1, 3 H); ^{13}C NMR ($(CD_3)_2CO$) δ 143.0, 132.9, 129.7, 127.7, 78.8, 69.0, 59.1, 32.9, 32.4, 25.0, 23.8, 14.3; TLC (EtOAc-hexane, 7:3) R_f 0.35. Anal. Calcd for $C_{14}H_{21}NO_4S$: C, 56.17; H, 7.07; N, 4.68. Found: C, 56.28; H, 6.97; N, 4.53.

(1*RS*,2*SR*,3*SR*)- and (1*RS*,2*SR*,3*RS*)-3-Ethyl-2-*n*-propyl-1,2-cyclobutanediol (13): 0.28 g, 87%; oil. The following spectra are of a 2:1 mixture of cyclobutanediols: ^1H NMR ($CDCl_3$) δ 4.04 (b), 3.86 (b), 3.72 (b), 3.52 (b), 3.05 (b), 2.18-2.23 (m), 2.01-2.05 (m), 1.78-1.84 (m), 1.05-1.58 (m, 8 H), 0.81-0.85 (m), 0.75 (m); ^{13}C NMR ($CDCl_3$) δ 79.3, 77.5, 70.3, 68.4, 45.7, 42.5, 39.6, 35.7, 33.8, 30.6, 22.9, 22.0, 16.6, 16.0, 14.44, 14.38, 11.9, 11.8; MS (LiCl added, m/z) 165 (MLi^+, 100), 141 ($[MH - H_2O]^+$, 45), 121 (48), 115 (64), 105 (75); HRMS calcd for MLi^+ 165.1467, found 165.1461; calcd for $[MH - H_2O]^+$ 141.1279, found 141.1282; TLC (EtOAc-hexane, 3:7) R_f 0.30.

***cis*-Bicyclo[4.2.0]octane-*cis*-1,8-diol (15)**: 0.26 g, 93%; mp 56-57 °C; ^1H NMR ($CDCl_3$) δ 4.46 (b, 1 H), 4.13 (b, 1 H), 3.88 (dd, J = 3.7, 4.9, 1 H), 2.30-2.36 (m, 1 H), 1.60-1.72 (m, 3 H), 1.15-1.53 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 73.3, 71.8, 38.3, 32.8, 28.5, 26.0, 22.0, 21.6; MS (LiCl added, m/z) 149 (MLi^+, 100), 125 (13); m/z 125 ($[MH - H_2O]^+$, 100, 107 (36); TLC (EtOAc-hexane, 3:7) R_f 0.14 [lit.[5c] mp 54-56 °C; ^1H NMR (CCl_4, 60 MHz) δ 4.6 (s, 2 H, OH), 3.8 (t, 1 H, CHOH), 1.0-2.7 (m, 11 H)]. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.71; H, 9.79.

(1*RS*,2*RS*,3*RS*)-3-((*tert*-Butyldimethylsilyl)oxy)-1,2-cyclobutanediol (17): 0.26 g, 75%; oil; ^1H NMR ($CDCl_3$) δ 4.24-4.29 (m, 2 H), 3.91 (dd, J = 6.0, 14.6, 1 H), 2.55 (d, J = 8.7, 1 H), 2.16 (d, J = 2.8, 1 H), 2.09 (dd, J = 8.3, 12.8, 1 H), 1.65-1.71 (m, 1 H), 0.88 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 75.7, 74.7, 64.7, 33.7, 25.7, 17.9, -4.8, -4.9; MS (LiCl added, m/z) 225 (MLi^+, 100); MS m/z 219 (MH^+, 100), 201 ($[MH - H_2O]^+$, 63); TLC (EtOAc-hexane, 2:8) R_f 0.17. Anal. Calcd for $C_{10}H_{22}O_3Si$: C, 55.00; H, 10.15. Found: C, 54.90; H, 10.29.

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Lithiation-Induced 1,3-Migrations of P^{IV} Groups from Heteroatom to the Naphthalene Ring†

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Ortho lithiation is an important method for the regiospecific construction of polysubstituted aromatics.[1] When the ortho-lithiation directing group is composed of an electronegative atom attached to a π-unsaturated group or coordinately unsaturated group, the lithiated species may undergo 1,3-migration to the ortho position on the aromatic ring.[2] Such metalation-induced 1,3-migrations are very common in the benzene systems and include the rearrangements of (i) arenesulfonamides of N-substituted anilines to N-substituted 2-aminodiaryl sulfones,[2,3] (ii) aryl o-carbamates to salicylamides,[4] (iii) o-bromophenyl esters to o-hydroxyaryl ketones,[5] (iv) aryl phosphate esters to 2-hydroxyaryl phosphonates,[6-10] and (v) (triarylsiloxy)benzenes to o-(trialkylsilyl)phenols.[11,12]

In spite of the significant amount of the work done on the metalation of monosubstituted naphthalenes, there are only two examples of such metalation-induced 1,3-migrations reported in the naphthalene series,[2] namely, the rearrangement of *N*-methyl-*N*-(2-naphthyl)-4-methylbenzenesulfonamide to *N*-methyl-3-[(4-methylphenyl)sulfonyl]-2-naphthylamine and the rearrangement of *N*-methyl-*N*-(1-naphthyl)-4-methylbenzenesulfonamide to *N*-methyl-2-[(4-methylphenyl)sulfonyl]-1-naphthylamine. The failure of (trialkylsiloxy)naphthalenes on treatment with *tert*-butyllithium to undergo rearrangement to (trialkylsilyl)naphthols[12] and the poor yield (11%) in the conversion of *N*-methyl-*N*-(1-naphthyl)-4-methylbenzenesulfonamide to *N*-methyl-2-[(4-methylphenyl)sulfonyl]-1-naphthylamine[2] may have contributed to the lack of interest in the metalation-induced rearrangements in the naphthalene systems. Continuing our interest in the phosphate-phosphonate rearrangements,[8] we report in this paper several examples of the lithiation-induced 1,3 O to C migrations of the P^{IV} groups in the naphthalene system, which occur in good yields.

Diethyl 1-naphthyl phosphate (1) on treatment with excess LDA underwent clean rearrangement to diethyl (1-hydroxy-2-naphthyl)phosphonate (2), which exhibited a ^{31}P signal at +24.2 ppm as expected of a phosphonate ester. Diethyl 1-naphthyl phosphate (1) exhibits a ^{31}P signal at -6.11. These phosphate-phosphonate rearrangements[8] are accompanied by a significant downfield shift in the ^{31}P NMR signal. The structure of 2 is based on the spectral data (see Experimental Section). In the proton NMR spectrum, 2 showed a doublet at 8.4 ppm with J = 7 Hz, which was assigned to the H-8 proton. The structure was further confirmed by ^{13}C NMR, which exhibited C_{8a} as a doublet with a P-C_{8a} three-bond coupling of 13.8 Hz and C_{4a} as a doublet with a P-C_{4a} four-bond coupling of 2.3 Hz. The one-bond P-C_2 coupling was 181.9

† This paper is dedicated to Prof. Carl David Gutsche on the occasion of his 70th birthday.

(1) For reviews, see: (a) Gschwend, H. W.; Rodriguez, H. *Org. React. (N.Y.)* **1979**, *26*, I. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (c) Narasimhan, N. S.; Mali, R. S. *Synthesis* **1983**, 957. (d) Narasimhan, N. S.; Mali, R. S. *Topics in Current Chemistry*; Springer Verlag: Berlin, 1986; Vol. 138, p 63. (e) Snieckus, V. *Bull. Soc. Chim. Fr.* **1988**, 67. (f) Snieckus, V. *Heterocycles* **1980**, *14*, 1649. (g) Snieckus, V. *Lect. Heterocycl. Chem.* **1984**, *7*, 95.

(2) Hellwinkel, D.; Lenz, R. *Chem. Ber.* **1985**, *118*, 66 and references cited therein.

(3) (a) Hellwinkel, D.; Supp, M. *Chem. Ber.* **1976**, *109*, 3749. (b) Shafer, S. J.; Closson, W. D. *J. Org. Chem.* **1975**, *40*, 889.

(4) (a) Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1937. (b) Skowronska-Ptasinska, M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1985**, *50*, 2690. (c) Mills, R. J.; Horvath, R. F.; Sibi, M. P.; Snieckus, V. *Tetrahedron Lett.* **1985**, 1145.

(5) (a) Miller, J. A. *J. Org. Chem.* **1987**, *52*, 323. (b) Hellwinkel, D.; Lammerzahl, F.; Hofmann, G. *Chem. Ber.* **1983**, 3375.

(6) Melvin, L. S. *Tetrahedron Lett.* **1981**, 3375.

(7) Cambie, R. C.; Palmer, B. D. *Aust. J. Chem.* **1982**, *35*, 827.

(8) Dhawan, B.; Redmore, D. (a) *J. Org. Chem.* **1984**, *49*, 4018; (b) *Synth. Commun.* **1985**, *15*, 411; (c) *J. Org. Chem.* **1986**, *51*, 179; (d) *Synth. Commun.* **1987**, *17*, 465; (e) *J. Chem. Res., Synop.* **1988**, 222; (f) *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *42*, 117; (g) *J. Chem. Res., Synop.* **1990**, 184.

(9) Heinicke, J.; Bohle, I.; Tzschach, A. *J. Organomet. Chem.* **1986**, *317*, 11.

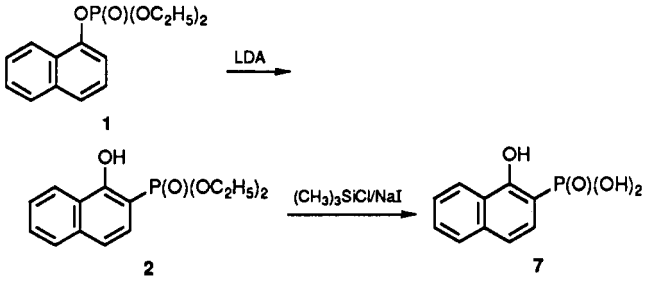
(10) Heinicke, J.; Kadyrov, R.; Kellner, K.; Nietzschmann, E.; Tzschach, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *44*, 209.

(11) (a) Speier, J. L. *J. Am. Chem. Soc.* **1952**, *74*, 1003. (b) Muslin, D. V.; Razuvaev, G. A.; Vavilina, N. N.; Vasileiskaya, N. S. *Izv. Akad Nauk SSSR, Ser. Khim.* **1975**, 182; *Chem. Abstr.* **1975**, *82*, 140253C. (c) Arai, I.; Park, K. H.; Daves, G. D. *J. Organomet. Chem.* **1976**, *121*, 25. (d) Heinicke, J.; Nietzschmann, E.; Tzschach, A. *J. Organomet. Chem.* **1983**, *232*, 1.

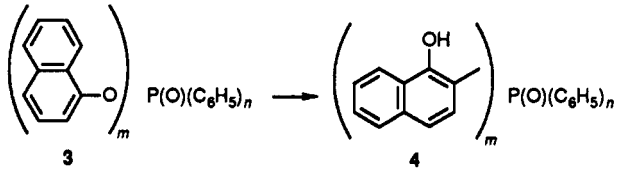
(12) Simchen, G.; Pfletschinger, J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 428.

0022-3263/91/1956-0833$02.50/0

Hz. There was no indication of the migration of P^{IV} group to C-8.

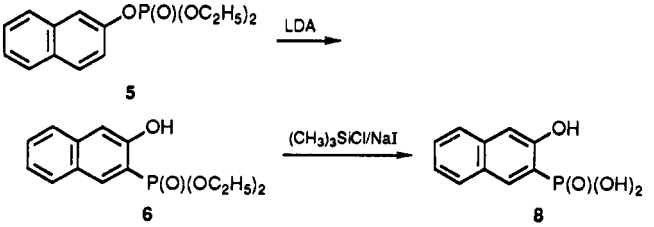


Treatment of 1-naphthyl diphenylphosphinate (**3a**) with excess LDA gave 2-(diphenylphosphinyl)-1-naphthol (**4a**) in 52% yield as a white crystalline solid, which exhibited a ^{31}P signal at +40.9 ppm. In the ^{13}C NMR of **4a**, the one-bond P–$C_{1'}$ coupling (phenyl ring) was 105.3 Hz and the one-bond coupling P–C_2 (naphthalene ring) was 106.9 Hz. These coupling constants agree with those observed for tris(2-hydroxyaryl)phosphine oxides.[8d] Di(1-naphthyl) phenylphosphonate (**3b**) when treated with excess LDA underwent double 1,3 O to C migrations of the P^{IV} groups, yielding bis(1-hydroxy-2-naphthyl)phenylphosphine oxide (**4b**) in 54% yield as a white crystalline solid. Tris(1-naphthyl) phosphate (**3c**) on similar treatment underwent triple 1,3 O to C migrations of the P^{IV} groups and was converted to tris(1-hydroxy-2-naphthyl)phosphine oxide (**4c**) in 65% yield.



a, $m = 1, n = 2$; **b**, $m = 2, n = 1$; **c**, $m = 3, n = 0$

Reaction of diethyl (2-naphthyl) phosphate (**5**) with excess LDA gave a crude product, which exhibited the ^{31}P signals at 21.2 and 25.3 ppm in a 2:1 intensity ratio. The major product was isolated and characterized as diethyl (3-hydroxy-2-naphthyl)phosphonate (**6**). In the ^1H NMR, it exhibited an H-I proton as a doublet at 8.04 ppm with $J_{P\text{-}H}$ = 16.5 Hz. In the ^{13}C NMR, C_{8a} appeared as a doublet with a three-bond P–C_{8a} coupling of 15.4 Hz and C_{4a} appeared as a doublet with a four-bond P–C_{4a} coupling of 2.3 Hz. No attempt was made to isolate the minor product, presumably the C-1 phosphonate. Lithiation of **5** probably occurs at both the 1 and the 3 positions, resulting in 1,3 O to C migration of the P^{IV} group to either of the metalated positions, giving mainly a mixture of two products. 2-Naphthol is, however, reported to undergo lithiation regioselectively at the 3-position.[13]



The phosphonate esters **2** and **6** were converted via trimethylsilyl esters into the corresponding phosphonic acids **7** and **8**. The phosphonic acids **7** and **8**, when allowed to stand dissolved in water, undergo decomposition slowly but were isolated as stable anilinium salts.

Lithiation-induced rearrangement of naphthalene derivatives **1**, **3a**, **3b**, and **3c**, under the conditions studied, is very regioselective with the P^{IV} group migrating to the 2-position on the naphthalene ring. This suggests that either the lithiation occurs preferentially at the 2-position and/or 1,3-migrations (migration of P^{IV} group to 2-position) are preferred over 1,4-migrations (migration of P^{IV} group to 8-position). These results are in agreement with the reports that 1-naphthyl carbamate[4a] and methoxymethyl ether of 5-methoxy-1-naphthol[14] undergo lithiation at the 2-position. Metalation of 1-naphthol is, however, reported to occur with poor regioselectivity.[13] It may also be noted that the regioselective outcome of lithiation in naphthalene derivatives is highly dependent on the conditions of lithiation. 1-Methoxynaphthalene, for example, can be made to undergo lithiation[15] selectively at the 1 or 8 position depending on the reaction conditions.

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Petrolite Corporation, Analytical Section. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ (unless stated otherwise) on a Varian Gemini-300 spectrometer, with operational frequencies of 300 (^1H) and 75 (^{13}C) MHz. Chemical shifts are given in ppm downfield from Me_4Si. J values (in hertz) are apparent, first-order coupling constants. ^{31}P NMR spectra were obtained in $CDCl_3$ solutions (unless stated otherwise) with H_3PO_4 (cap.) as external standard on a JEOL FX-60 spectrometer operating at 24.15 MHz. Anhydrous tetrahydrofuran (THF) (99.9%) was purchased from Aldrich and used as such.

Diethyl (1-Hydroxy-2-naphthyl)phosphonate (2). *n*-Butyllithium (62.5 mL, 1.6 M) was added to a solution of diisopropylamine (10.1 g, 100 mmol) in dry THF (40 mL) at −78 °C under a nitrogen atmosphere. After 30 min, a solution of diethyl 1-naphthyl phosphate[16] (1) (14.0 g, 50 mmol) in dry THF (40 mL) was added slowly with the help of a syringe. A white precipitate was formed. After 1 h at −78 °C, the reaction mixture was warmed to room temperature. The white precipitate dissolved, yielding a red solution. After 3 h at room temperature, the reaction mixture was poured over a mixture of 250 mL of saturated aqueous NH_4Cl and 300 mL of CH_2Cl_2. The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated to yield **2** as a slightly yellow liquid. The yield of twice-distilled **2** was 10.5 g (75%), colorless liquid, bp 170 °C (0.5 mm): ^{31}P NMR δ +24.2; ^1H NMR δ 1.25 (t, 7 Hz, 6 H, CH_3), 3.90–4.20 (m, 4 H, CH_2), 7.25–7.32 (m, 2 H, Ar), 7.40–7.54 (m, 2 H, Ar), 7.68 (d, 7 Hz, 1 H, Ar), 8.40 (d, 7.5 Hz, 1 H, H-8), 11.35 (bs, 1 H, OH); ^{13}C NMR δ 16.22 (d, 6.4 Hz, CH_3) 62.85 (d, 4.5 Hz, CH_2), 100.9 (d, 181.9 Hz, C_2), 119.8 (d, 13.3 Hz, C_4), 124.0, 125.3 (d, 13.8 Hz, C_{8a}), 125.9 (d, 6.6 Hz, C_3), 126.4, 128.0, 129.6, 137.5 (d, 2.3 Hz, C_{4a}), 161.7 (d, 7.6 Hz, C_1).

Anal. Calcd for $C_{14}H_{17}O_4P$: C, 60.00; H, 6.07; P, 11.07. Found: C, 60.12; H, 6.37; P, 11.14.

2-(Diphenylphosphinyl)-1-naphthol (4a). *n*-Butyllithium (12 mL, 2.5 M) was added to a solution of diisopropylamine (3.03 g, 30 mmol) in dry THF (25 mL) at −78 °C under an argon atmosphere. After 30 min, a solution of 1-naphthyl diphenylphosphinate[17] (**3a**) (5.16 g, 15 mmol) in dry THF (30 mL) was added with the help of a syringe. The reaction mixture was stirred at −78 °C for 1 h when an orange precipitate was formed. The reaction mixture was next warmed to room temperature. The orange precipitate dissolved and after some time a yellow precipitate separated out. After 2 h at room temperature, the reaction mixture was added to dilute HCl (85 mL water added to 15 mL

(13) Coll, G.; Morey, J.; Costa, A.; Saa, J. M. *J. Org. Chem.* **1988**, *53*, 5345.

(14) Kawikawa, T.; Kubo, I. *Synthesis* **1986**, 431.

(15) (a) Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, *20*, 251. (b) Narasimhan, N. S.; Mali, R. S. *Tetrahedron* **1975**, *31*, 1005.

(16) Kenner, G. W.; Williams, N. R. *J. Chem. Soc.* **1955**, 522.

(17) Berlin, K. D.; Austin, T. H.; Nagabhushanam, M. *J. Org. Chem.* **1965**, *30*, 1267.

of concentrated HCl). The reaction mixture was next extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated to yield 2-(diphenylphosphinyl)-1-naphthol (**4a**) as a white solid. The yield of **4a** after crystallization from methylene chloride/hexanes was 2.7 g (52%), mp 167 °C: ^{31}P NMR δ + 40.6; ^1H NMR δ 6.85–7.90 (m, 15 H, Ar), 8.35–8.50 (m, 1 H, Ar), 12.30 (b, 1 H, OH); ^{13}C NMR δ 102.6 (d, 106.9 Hz, C_2), 119.1 (d, 12.6 Hz, C_4), 123.8, 126.2 (d, 9 Hz, C_{8a}), 126.4, 126.6 (d, 10.6 Hz, C_3), 127.8, 129.2 (d, 12.4 Hz, $C_{3'}$), 129.4, 132.5 (d, 105.3 Hz, $C_{1'}$), 132.5 (d, 10.4 Hz, $C_{2'}$), 133.0 (d, 2.9 Hz, $C_{4'}$), 136.9 (C_{4a}), 163.3 (d, 2.9 Hz, C_1).

Anal. Calcd for $C_{22}H_{17}O_2P$: C, 76.74; H, 4.94; P, 9.01. Found: C, 76.43; H, 4.92; P, 9.06.

Bis(1-hydroxy-2-naphthyl)phenylphosphine Oxide (4b). *n*-Butyllithium (21.68 mL, 2.5 M) was added to a solution of diisopropylamine (5.47 g, 54.2 mmol) in dry THF (35 mL) at −78 °C under an argon atmosphere. After 30 min, a solution of di(1-naphthyl) phenylphosphinate[18] (**3b**) (5.55 g, 13.5 mmol) in dry THF (35 mL) was added. After being stirred at −78 °C for 1 h, the reaction mixture was warmed to room temperature. After 2 h, the reaction mixture was added to dilute HCl (85 mL of water added to 15 mL of concentrated HCl). The reaction mixture was extracted with ether (150 mL). The ether extract was washed with water, dried (Na_2SO_4), and evaporated to yield **4b** as a white solid. The yield of **4b** after crystallization from methylene chloride/hexanes was 3.0 g (54%), mp 182–183 °C: ^{31}P NMR δ +51.4; ^1H NMR δ 7.0–7.9 (m, 15 H, Ar), 8.3–8.5 (m, 2 H, Ar), 11.6 (s, 2 H, OH); ^{13}C NMR δ 102.7 (d, 108.3 Hz, C_2), 119.6 (d, 12.6 Hz, C_4), 123.8, 126.2 (d, 10.8 Hz, C_3), 126.7, 127.9, 129.5 (d, 13.1 Hz, $C_{3'}$), 129.7, 132.4 (d, 106.3 Hz, $C_{1'}$), 132.7 (d, 11.6 Hz, $C_{2'}$), 133.8 (d, 2.8 Hz, $C_{4'}$), 137.1, 163.0 (d, 3.0 Hz, C_1).

Anal. Calcd for $C_{26}H_{19}O_3P$: C, 76.09; H, 4.63; P, 7.56. Found: C, 76.48; H, 4.87; P, 7.60.

Tris(1-hydroxy-2-naphthyl)phosphine Oxide (4c). *n*-Butyllithium (21.68 mL, 2.5 M) was added to a solution of diisopropylamine (5.47 g, 54.2 mmol) in dry THF (35 mL) at −78 °C under an argon atmosphere. After 30 min, a solution of 1-naphthyl phosphate[19] **3c** (4.30 g, 9 mmol) in dry THF (35 mL) was added. The reaction mixture was stirred at −78 °C for 1 h and then warmed to room temperature. After 2 h, the reaction mixture was added to dilute HCl (85 mL of water added to 15 mL concentrated HCl). The reaction mixture was next extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated to yield crude **4c** as a white solid. The yield of **4c** after crystallization from ethanol was 2.8 g (65%), mp 240 °C: ^{31}P NMR δ +53.70; ^1H NMR δ 7.05–7.90 (m, 18 H, Ar), 8.35–8.50 (m, 3 H, Ar), 10.55 (b, 3 H, OH); ^{13}C NMR δ 104.3 (d, 108.7 Hz, C_2), 120.2, (d, 12.8 Hz, C_4), 123.8, 125.9, 125.9 (d, 10.6 Hz, C_3), 126.8, 128.0, 129.9, 137.3, 161.4 (d, 2.6 Hz, C_1).

Anal. Calcd for $C_{30}H_{21}O_4P$: C, 75.63; H, 4.41; P, 6.51. Found: C, 75.22; H, 4.52; P, 6.46.

Diethyl (3-Hydroxy-2-naphthyl)phosphonate (6). Starting with 14.0 g of diethyl 2-naphthyl phosphate[16] (**5**) and following the procedure as for **2**, the crude product was obtained as a thick oil. ^{31}P NMR of the crude product exhibited signals at δ 21.2 and 25.3 in 2:1 ratio. On standing, **6** separated as a solid in the thick oil. **6** was collected by filtration and crystallized from hexanes as a white solid, 5.5 g (39%), mp 114 °C: ^{31}P NMR δ +21.2; ^1H NMR δ 1.34 (t, 7 Hz, 6 H, CH_3), 4.0–4.3 (m, 4 H, CH_2), 7.26–7.36 (m, 2 H, Ar), 7.48 (app t, 8.5 Hz, 1 H), 7.72 (d, 8.5 Hz, 1 H), 7.78 (d, 8 Hz, 1 H), 8.04 (d, 16.5 Hz, 1 H), 10.0 (s, 1 H, OH); ^{13}C NMR δ 16.28 (d, 6.5 Hz, CH_3), 63.23 (d, 5.0 Hz, CH_2), 112.0 (d, 11.3 Hz, C_4), 112.9 (d, 179.4 Hz, C_2), 124.4, 127.0, 127.8 (d, 15.4 Hz, C_{8a}), 129.1, 129.2, 134.7 (d, 5.9 Hz, C_1), 138.2 (d, 2.3 Hz, C_{4a}), 157.3 (d, 7.7 Hz, C_3).

Anal. Calcd for $C_{14}H_{17}O_4P$: C, 60.00; H, 6.07; P, 11.07. Found: C, 60.41; H, 6.21; P, 11.11.

(1-Hydroxy-2-naphthyl)phosphonic Acid (7). To a mixture of diethyl (1-hydroxy-2-naphthyl)phosphonate (**2**) (2.8 g, 10 mmol), acetonitrile (20 mL), and sodium iodide (4.5 g) under nitrogen was added chlorotrimethylsilane[8a] (3.25 g). The reaction mixture was stirred at room temperature for 16 h and then at 40 °C for 1 h. It was next filtered to remove NaCl and volatiles were removed on the rotary evaporator. Chloroform (30 mL) was added to the residue when some more NaCl precipitated out. After the removal of NaCl by filtration, chloroform was removed on the rotary evaporator. Water (20 mL) was added to the crude silyl ester. After 15 min of stirring at room temperature, the aqueous layer was separated and evaporated to dryness on the rotary evaporator. Acetonitrile (25 mL) was added to the residue and the mixture was evaporated to obtain a slightly yellow solid. The solid residue was stirred for 15 min with methylene chloride (40 mL) and then collected by filtration. The yield of white solid **7** was 2.0 g (89%); ^{31}P NMR (D_2O/H_3PO_4 cap.) +16.6. The crude acid (0.5 g) was dissolved in ethanol (20 mL) and aniline (0.36 g) was added. The mixture was warmed, and, on cooling, the anilinium salt of **7** crystallized out slowly as a white solid, 0.43 g (61%), mp 168–169 °C: ^{31}P NMR (DMSO/H_3PO_4 cap.) δ +17.3; ^1H NMR (DMSO/Me_4Si/one drop D_2O) δ 6.84–6.92 (m, 3 H, Ar), 7.16–7.58 (m, 6 H, Ar), 7.8 (app d, 7.5 Hz, 1 H, Ar), 8.2 (app d, 8 Hz, 1 H, H-8); ^{13}C NMR (DMSO/Me_4Si) δ 108.4 (d, 175.1 Hz, C_2), 115.8, 118.2, 118.35 (d, 13.0 Hz C_4), 123.1, 124.5 (d, 12.9 Hz, C_{8a}), 125.8, 127.3 (d, 6.7 Hz, C_3), 127.8, 128.4, 129.3, 136.1 (d, 2.3 Hz, C_{4a}), 146.1, 157.8 (d, 7.0 Hz, C_1).

Anal. Calcd for $C_{16}H_{16}NO_4P$; C, 60.57; H, 5.05; N, 4.42; P, 9.78. Found: C, 60.50; H, 5.10; N, 4.46; P, 9.94.

(3-Hydroxy-2-naphthyl)phosphonic Acid (8). Starting with 1.87 g of **6**, the yield of the crude acid **8** was 1.30 g (87%). For characterization, it was converted into the anilinium salt, yield 73%, white solid, mp 213–214 °C: ^{31}P NMR (DMSO/H_3PO_4 cap.) +13.4; ^1H NMR (DMSO/Me_4Si/one drop D_2O) 6.8–6.9 (m, 3 H, Ar), 7.1–7.2 (m, 3 H, Ar), 7.3 (t, 7 Hz, 1 H, Ar), 7.5 (t, 7 Hz, 1 H, Ar), 7.7 (d, 8 Hz, 1 H, Ar), 7.8, (d, 8 Hz, 1 H, Ar), 8.1 (d, 14.5 Hz, 1 H, Ar); ^{13}C NMR (DMSO/Me_4Si) δ 109.6 (d, 9.1 Hz), 116.4, 118.9, 121.6 (d, 173.2 Hz, C_2), 123.4, 126.2, 127.2 (d, 14.0 Hz, C_{8a}), 127.9, 128.7, 129.4, 133.8 (d, 4.6 Hz), 136.5, 145.1, 156.6 (d, 4.7 Hz, C_3).

Anal. Calcd for $C_{16}H_{16}NO_4P$: C, 60.57; H, 5.05; N, 4.42; P, 9.78. Found: C, 60.25; H, 5.12; N, 4.32; P, 9.83.

(18) Campbell, J. R.; Hatton, R. E. U.S. Patent 3,071,609; *Chem. Abstr.* **1963**, *58*, 11401 g.
(19) Krishnakumar, V. V.; Sharma, M. M. *Synthesis* **1983**, 558.

Synthesis of Substituted Cyclic 1,3-Dienes via Selective 1,4-Elimination of Benzenesulfinic Acid from Allylic Phenyl Sulfones

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Conjugated dienes are useful substrates in organic synthesis. The classical use has been cycloaddition, but recently metal-mediated additions to these substrates have attracted considerable interest.[2] In our projects on palladium-catalyzed oxidation of conjugated dienes, there was a demand for specifically substituted conjugated dienes.[3] In our first approach to prepare these substrates, we studied alkylation of allylic aryl sulfoxides and subsequent thermal elimination.[4,5] However, this approach resulted

(1) (a) University of Uppsala. (b) University of Notre Dame.
(2) Bäckvall, J. E. "Metal-Mediated Additions to Conjugated Dienes" in *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; Jai Press: Greenwich, CT, 1989; Vol. 1, pp 135–175.
(3) (a) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619. (b) Bäckvall, J. E.; Andersson, P. G.; Vågberg, J. O. *Tetrahedron Lett.* **1989**, *30*, 137.
(4) For thermal elimination of sulfoxides, see: (a) Tanikaga, R.; Nozaki, Y.; Nishida, M.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 729. (b) Huynh, C.; Julia, S. *Synth. Commun.* **1977**, *7*, 103. (c) Trost, B. M.; Leung, K. K. *Tetrahedron Lett.* **1975**, 4197. (d) Trost, B. M. *Chem. Rev.* **1978**, *78*, 363.

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