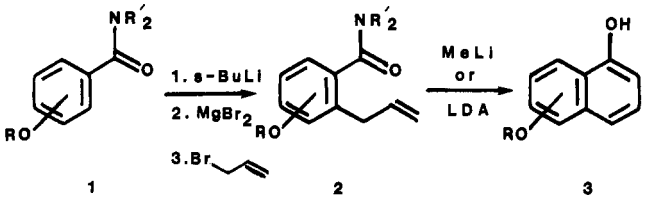
Communications

Anionic Aromatic Ring Annelation of *o*-Allylbenzamides. Regiospecific Synthesis of Naphthols and Naphthoquinones

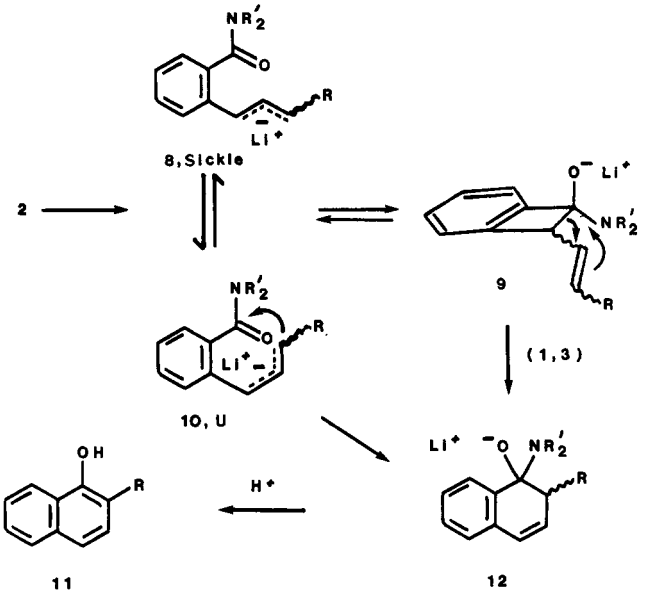
Summary: *o*-Allylbenzamides **2**, available from **1** by directed ortho metalation or transition metal catalyzed cross-coupling reactions, undergo MeLi-induced cyclization to give 1-naphthols **3**, some of which are immediate precursors for oxygenated naphthoquinones **6** and **7**.

Sir: Aromatic annelation onto benzene derivatives is usually achieved by several-step sequences which are initiated from mono- or 1,2-disubstituted benzene precursors by diverse cationic,[1] anionic,[2] and cycloaddition[3,4] processes and which generally require dehydrogenation steps.[5] As a contribution to the recent activity in aromatic ring synthesis,[6] we report on a new one-step anion-induced benzoannelation method, **2** → **3**, which allows regiospecific access to substituted naphthols. The scope and utility



of this method is reflected in (a) the convenient derivation of a variety of substituted *o*-allylbenzamides **2** from **1** via the directed ortho metalation[7,8] and transition metal catalyzed cross-coupling[9] protocols, (b) the modification of **2** into *o*-(silylallyl)benzamides to achieve an intramolecular amide Peterson olefination (Table I, entry 9),[10] and (c) the ready conversion of **4** into certain poorly accessible naphthoquinones **6** and **7** whose significance in natural product synthesis is well documented.[11]

Scheme I



Treatment of *N,N*-diethyl-*o*-allylbenzamide[7] with 2.2 equiv of MeLi[12] (THF/−78 °C → room temperature/8 h) afforded 1-naphthol in high yield (Table I, entry 1). Although other bases (LDA, *sec*-BuLi, MeMgI) were examined, the MeLi conditions as defined above were found to be optimal for the anionic cyclization. A number of other *o*-allylbenzamides were similarly cyclized to substituted naphthols in good yields (entries 3–7). A steric effect to cyclization, potentially ascribable to the bulk of the amide substituent, is evident from comparison of entries 2 and 3 although this appears not to be as detrimental a factor for a number of the other oxygenated benzamides.

To circumvent the failure to obtain *o*-crotylbenzamides via the directed metalation–transmetalation procedure,[7] the transition metal catalyzed cross-coupling tactic of

(1) Cyclization of monosubstituted benzenes: Friedel–Crafts-type reactions (Sethna, S. In "Friedel–Crafts and Related Reactions"; Olah, G. A., Ed.; Wiley Interscience: New York, 1964; Vol. III, Part 2, p 911). For a direct method, see: Loozen, H. J. J. *J. Org. Chem.* **1975**, *40*, 520.

(2) (a) Classical (e.g., Dieckmann) cyclization of 1,2-disubstituted benzenes. For a direct method based on α-tosyl-*o*-tolualdehydes, see: Wildeman, J.; Borgen, P. C.; Pluim, H.; Rouwette, P. H. F. M.; van Leusen, A. M. *Tetrahedron Lett.* **1978**, 2213. (b) Cyclization of phenols: Murphy, W. S.; Wattanasin, S. *Chem. Soc. Rev.* **1983**, *12*, 213. (c) Parham-type cycloacylation of *ortho*-lithiated monosubstituted benzene: Parham, W. E.; Bradsher, C. K. *Acc. Chem. Res.* **1982**, *15*, 300. (d) Phthalide anion based annelations: Broom, N. J. P.; Sammes, P. G. *J. Chem. Soc., Perkin Trans 1* **1981**, 465. Hauser, F. M.; Mal, D. *J. Am. Chem. Soc.* **1984**, *106*, 1098 and references therein.

(3) (a) Via isobenzofurans and related intermediates: Wiersum, U. E. *Aldrichimica Acta* **1981**, *14*, 53 and references to reviews cited therein. For recent examples, see: Keay, B. A.; Rajapaksa, D.; Rodrigo, R. *Can. J. Chem.* **1984**, *62*, 1093. Beak, P.; Chen, C.-W. *Tetrahedron Lett.* **1983**, 2945. Levy, L. A.; Kumar, V. P. S. *Ibid.* **1983**, 1221. Makhlouf, M. A.; Rickborn, B. *J. Org. Chem.* **1981**, *46*, 2734. Contreras, L.; MacLean, D. B.; Faggiani, R.; Lock, C. J. L. *Can. J. Chem.* **1981**, *59*, 1247 and references therein. (b) Via benzynes: Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes"; Academic Press: New York, 1967; p 208. (c) Via *o*-quinodimethanes: Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. For an extensive list of references, see: Moder, K. P.; Leonard, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 2613. (d) Via 2-pyrones: Corey, E. J.; Kozikowski, A. P. *Tetrahedron Lett.* **1975**, 2389. (e) From styrene derivatives: Kita, Y.; Yasuda, H.; Tamura, O.; Tamura, Y. *Ibid.* **1984**, 1813 and references therein. (f) Via homophthalic anhydride anions: Tamura, Y.; Sasho, M.; Nakagawa, K.; Tsugoshi, T.; Kita, Y. *J. Org. Chem.* **1984**, *49*, 473.

(4) A very general annelation methodology based on Diels–Alder cycloaddition to benzoquinones and requiring minor modification to achieve the aromatic oxidation state is also available; see: Roberge, G.; Brassard, P. *J. Org. Chem.* **1981**, *46*, 4161. Brisson, C.; Brassard, P. *Ibid.* **1981**, *46*, 1810 and references therein.

(5) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317.

(6) For an excellent review, see: Bamfield, P.; Gordon, P. F. *Chem. Soc. Rev.* **1984**, *13*, 441. See also: Tius, M. A.; Thurkauf, A.; Truesdell, J. W. *Tetrahedron Lett.* **1982**, 2819 and references therein.

(7) Sibi, M. P.; Miah, M. A. J.; Snieckus, V. *J. Org. Chem.* **1984**, *49*, 737.

(8) Review: Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.

(9) Minato, A.; Tamao, K.; Hayashi, T.; Suzuki, K.; Kumada, M. *Tetrahedron Lett.* **1981**, 5319.

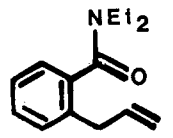
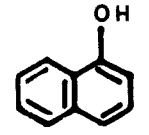
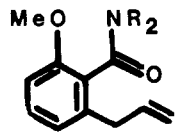
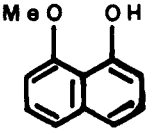
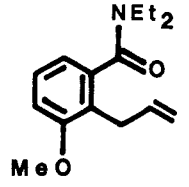
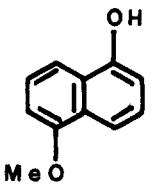
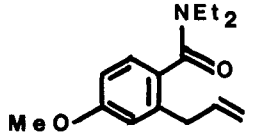
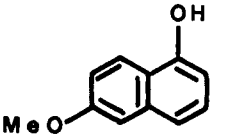
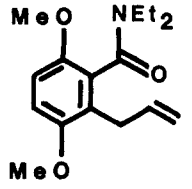
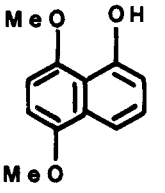
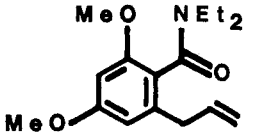
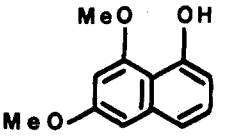
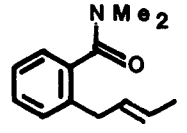
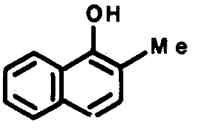
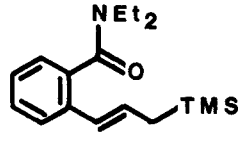
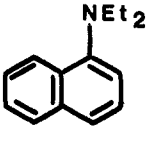
(10) To the best of our knowledge, this is the first example of an intramolecular Peterson olefination involving an amide acceptor. For intermolecular cases, see: Agawa, T.; Ishikawa, M.; Komatsu, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1205. See also: Woodbury, R. P.; Rathke, M. W. *Tetrahedron Lett.* **1977**, 709.

(11) See, for example, (a) anthracyclinones: Parker, K. A.; Kallmerten, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 5881. (b) Anthraquinones, ref 4. (c) Naphthoquinones, ref 4 and: Naruta, Y.; Uno, H.; Muruyama, K. *Chem. Lett.* **1982**, 609.

(12) Treatment of tertiary benzamides with MeLi usually produces acetopheones: Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M. *Synthesis* **1984**, 228.

0022-3263/86/1951-0271$01.50/0

Table I. Synthesis of Naphthols from *o*-Allylbenzamides

entry	substrate	product	yield,[a,b] %	mp [bp], °C
1			86 (65)	93-95[c] (hexane)
				
2	R = Et		35 (16)	45-46[d] (petroleum ether)
3	R = Me		81	
4			90 (58)	136-138[e] (CH_2Cl_2-hexane)
5			64	83-84[f] (petroleum ether)
6			77 (37)	98-100[g] (CH_2Cl_2-hexane)
7			62	83-85[h] (CCl_4-petroleum ether)
8			50	58-59[i] (Et_2O-petroleum ether)
9			35	[155-158 (30 torr)[j]]

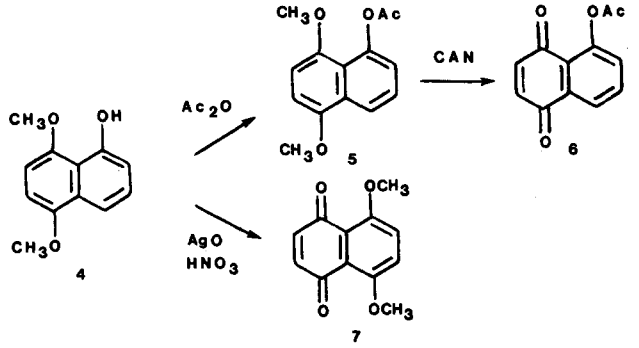
[a] Yields of purified (chromatographed and crystallized) material. [b] Yields in parentheses correspond to those obtained using 2.2 equiv of LDA. [c] Franzen, H.; Kempf, H. *Chem. Ber.* **1917**, *50*, 101. [d] Lit. mp 47 °C: Boeseken, J.; Smitt, L. G. *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 125. [e] Lit. mp 140-141 °C: see ref 11a. [f] Lit. mp 85 °C: Byrde, R. J. W.; Downing, D. F.; Woodcock, D. *Biochem. J.* **1954**, *72*, 344. [g] Lit. 103-104 °C: Asano, M.; Hase, J. *J. Pharm. Soc. Jpn.* **1943**, *63*, 83. [h] Lit. mp 86 °C: Hardegger, E.; Rigassi, N.; Seres, J.; Egli, Ch.; Mueller, P.; Fitzi, K. O. *Helv. Chim. Acta* **1963**, *46*, 2543. [i] Lit. mp 61 °C: Horii, Z.-i.; Tanaka, T.; Murukami, Y. *Pharm. Bull.* **1957**, *5*, 82; *Chem. Abstr.* **1957**, *51*, 17859a. [j] Lit. bp 155-165 °C (30 torr): Emerson, W. M. S. U.S. Patent 2 414 031, **1947**; *Chem. Abstr.* **1947**, *41*, 2439e.

Kumada[9] was adapted. Thus metal halogen exchange (*n*-BuLi/THF/−100 °C) of *N,N*-dimethyl-*o*-bromobenzamide, followed by transmetallation ($MgBr_2$·Et_2O/−78 °C) and coupling with crotyl bromide in the presence of $NiCl_2(PPh_3)_2$ gave the required *N,N*-dimethyl-*o*-crotylbenzamide in 70% yield.[13] When this compound was subjected to the MeLi-mediated benzoannelation conditions, 2-methyl-1-naphthol was obtained (entry 8). The

(13) The reason for the failure of the corresponding cross-coupling reaction using the *o*-MgBr species derived by directed ortho lithiation–transmetalation[7] is presently unknown.

failure to detect this product from the cyclization attempt of the corresponding *N,N*-diethyl-*o*-crotylbenzamide suggests the operation of an even greater steric factor compared to that observed for the *o*-allyl analogue (entry 2). The *o*-allyl silane (entry 9), prepared in 72% yield by metalation–silylation of *N,N*-diethyl-*o*-allylbenzamide [(1) *sec*-BuLi/TMEDA/THF/−78 °C; (2) Me_3SiCl], was treated under the MeLi cyclization conditions described above to furnish the amide Peterson olefination product,[10] 1-(dimethylamino)naphthalene (entry 9).

Aside from its inherent value, the anionic cyclization also establishes a direct synthetic link between readily available benzamide derivatives and oxygenated naphthoquinones. Illustrative of this is the dual character of **4**, which by direct oxidation (AgO/HNO_3/acetone)[14] yields naphthoquinone **7**[15] in 31% yield and by initial conversion to its



acetate **5** (95%) followed by oxidation ($Ce(NH_4)_2(NO_3)_6$/MeCN–H_2O)[16] affords juglone acetate (**6**)[17] in 96% yield. These routes are highly competitive with previous synthetic methods devised for these valuable naphthoquinones.[18]

A tentative mechanistic rationalization (Scheme I) for the observed benzoannelation involves the initial formation of equilibrating anions whose energy minimum is best represented by the sickle-shaped species **8**.[19] Formation of naphthol **11** may occur via intermediate **12** by two pathways: (a) direct cyclization from the obligatory U-shaped anion **10** or (b) via the 2-vinylbenzocyclobutane carbinolamine alkoxide **9** followed by a [1,3]-sigmatropic rearrangement.[20,21] The formation of the 1-aminonaphthalene (entry 9) requires a cis alkoxide–Me_3Si relationship in **12**, R = Me_3Si to be consistent with the demonstrated stereochemical requirement for the Peterson olefination.[22] The rotational barrier between **8** and **10** (C_1–C_2 *E* to *Z* interconversion) appears to be prohibitive.[23] On the other hand, compelling evidence for the intermediacy of analogous 2-vinylbenzocyclobutanol alkoxide species in the reaction of benzyne with dienolates to form naphthalene derivatives has been provided by labeling and product analysis studies.[24] Complementary evidence for species **9** is currently being sought.

On the basis of these preliminary results, the anionic aromatic annelation process should be useful for regiospecific construction of naphthol and naphthoquinone derivatives. In addition, it may prove to be adaptable to the synthesis of naphthoquinone antibiotics.[25] Synthetic and mechanistic aspects of this reaction are under investigation.[26,27]

Registry No. **4**, 91963-30-3; **5**, 99618-32-3; **6**, 5196-28-1; **7**, 15013-16-8; *N,N*-diethyl-*o*-allylbenzamide, 88440-83-9; 6-methoxy-*N,N*-diethyl-2-allylbenzamide, 88440-84-0; 6-methoxy-*N,N*-dimethyl-2-allylbenzamide, 99618-27-6; 3-methoxy-*N,N*-diethyl-2-allylbenzamide, 88440-85-1; 4-methoxy-*N,N*-diethyl-2-allylbenzamide, 99618-28-7; 3,6-dimethoxy-*N,N*-diethyl-2-allylbenzamide, 88440-86-2; 4,6-dimethoxy-*N,N*-diethyl-2-allylbenzamide, 99618-29-8; *N,N*-dimethyl-*o*-crotylbenzamide, 99618-30-1; *N,N*-diethyl-o-(3-(trimethylsilyl)allyl)benzamide, 99618-31-2; 1-naphthol, 90-15-3; 8-methoxy-1-naphthol, 3588-75-8; 5-methoxy-1-naphthol, 3588-80-5; 6-methoxy-1-naphthol, 22604-07-5; 6,8-dimethoxy-1-naphthol, 51114-96-6; 2-methyl-1-naphthol, 7469-77-4; 1-(diethylamino)naphthalene, 84-95-7; *N,N*-dimethyl-*o*-bromobenzamide, 54616-47-6; crotyl bromide, 4784-77-4.

(14) Synder, C. D.; Rapoport, H. *J. Am. Chem. Soc.* **1972**, *94*, 227.
(15) Mp 152–155 °C (lit. mp 157 °C), cf.: Bruce, D. B.; Thomson, R. H. *J. Chem. Soc.* **1955**, 1089.
(16) (a) Hannan, R. L.; Barber, R. B., Rapoport, H. *J. Org. Chem.* **1979**, *44*, 2153. (b) Jacob, P., III; Callery, P. S.; Shulgin, A. T.; Castagnoli, N., Jr. *Ibid.* **1976**, *41*, 3627.
(17) Mp 150–151 °C (lit. mp 153–154 °C), cf.: Fieser, L. F.; Dunn, J. T. *J. Am. Chem. Soc.* **1937**, *59*, 1016.
(18) Muller, E., Ed. "Methoden der Organische Chemie (Houben-Weyl)"; Thieme Stuttgart, Vol. VII/3a, Part 1, pp 71, 78.
(19) Based on the established *E* geometry of phenylallylithium: (a) Sandel, V. R.; McKinley, S. V.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 495. For a review, see: (b) Bates, R. B.; Ogle, C. A. "Carbanion Chemistry"; Springer-Verlag: Berlin, 1983; pp 23, 40.
(20) For alkoxy-accelerated [1,3]-sigmatropic shifts of 2-vinylcyclobutanols, see: Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479. Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943. A concerted mechanism for the conversion of **9** into **12** may involve the trans or cis alkoxide–vinyl isomers of **9** by suprafacial-inversion and -retention pathways.
(21) For a potentially related thermal rearrangement of silyl cyanohydrins of vinylcyclobutanones, see: Byers, J. H.; Spencer, T. A. *Tetrahedron Lett.* **1985**, 713.
(22) Weber, W. P. "Silicon Reagents in Organic Synthesis"; Springer-Verlag: Berlin, 1983; p 58.
(23) The *Z* isomer of phenylallyllithium corresponding to **10** cannot be detected in THF solution at 5 °C.[19a] The carbamoyl substituent would be expected to increase the rotational barrier discouraging equilibration to **10**. However, coordination effects between the proximate carbamoyl and the allyllithium (σ- or π-bonded) groups and ultimate aromatization may constitute the overall driving force for the reaction.
(24) Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1377. Brunet, J. J.; Essiz, M.; Caubere, P. *Tetrahedron Lett.* **1974**, 871.
(25) Semmelhack, M. F.; Bodurow, C.; Baum, M. *Tetrahedron Lett.* **1984**, 3171.
(26) All new compounds show analytical and spectral (IR, NMR, MS) data in full accord with the assigned structures.
(27) We are grateful to NSERC Canada and Merck Frosst for financial support of our synthetic programs. We are indebted to Professor John E. Baldwin for reference 20.

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Phase-Transfer-Catalyzed Conversion of Alkynes to Lactones Induced by Manganese Carbonyl Complexes

Summary: Alkynes react with methyl iodide, bromopentacarbonylmanganese (or dimanganese decacarbonyl), and carbon monoxide, under phase-transfer catalysis conditions, to give γ-butyrolactones; the reaction conditions are mild [35 °C (1 atm)], and the process is a regiospecific one.

Sir: Although much work has been done on the application of phase-transfer catalysis to organometallic chemistry,[2] little has involved the utilization of manganese complexes. The binuclear manganese complex $Mn_2(CO)_9Br^-$ is formed

(1) John Simon Guggenheim Fellow, 1985–1986.
(2) Alper, H. *Fundam. Res. Homogeneous Catal.* **1984**, *4*, 79; *Adv. Organomet. Chem.* **1981**, *19*, 183.

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