A wide variety of aromatic (entries 1–20), condensed aromatic (entries 21–25), and heterocyclic (entries 26–33) derivatives participate in this reaction (Table I). The required solvent for carbamate coupling is Et_2O (THF fails, PhH has limited value) while triflate coupling proceeds in Et_2O or THF with similar facility. $Ni(acac)_2$ catalyst provided consistent results while the more expensive $NiCl_2(dppp)$ gave less clean reactions (especially with carbamates) and Pd(0) catalysts were totally ineffective. Methyl, $TMSCH_2$, and aryl Grignards are useful coupling partners while allyl and benzyl Grignards, as observed frequently in Ni-catalyzed reactions,[6b] fail or give complex mixtures. A major difference is observed with *n*-BuMgCl: whereas triflates (entry 16) undergo smooth coupling, the corresponding carbamates (entry 17) give reductive products, undoubtedly a result of β-hydrogen elimination.[6b] This difference, perhaps a reflection of the relatively faster rate of triflate over carbamate oxidative addition to Ni(0), is of considerable synthetic value as illustrated by a sequence leading to difficult to access 2,3-disubstituted naphthalenes (Scheme II). Thus, directed metalation-mediated consecutive introduction of carbamoyl and silyl electrophiles into carbamate **5** leads to **6** which, upon treatment with *i*-PrMgCl/$Ni(acac)_2$ gives **7**, demonstrating the latent DMG character of the $OCONEt_2$ group. Inspection of carbamate and triflate reactivity patterns indicates the operation of as yet poorly understood steric and electronic effects. Thus, an *o*-phenyl group retards reactivity for both the diethyl carbamate and triflate (entries 1 and 3), while the dimethyl carbamate (entry 2) gives an excellent yield of product, a result which, however, is compromised by its inadequate DMG character.[2] Comparison of more highly hindered cases suggests significant synthetic advantage of using triflates over carbamates (entries 14 vs 13).

In the carbamate series, *o*-oxygen (entry 4), *m*-oxygen (entries 6, 7), and *m*-nitrogen (entry 8) EDGs give good results except the *m*-carbamate (entry 9). *o*- and *p*-EWGs enhance rates considerably and lead to good yields of benzylsilane products (entries 5, 11, 12). Entry 10 documents the preferential triflate over carbamate coupling, a result of practical synthetic value.

Comparison of entries 7 vs 10 reveals that either acid (OMOM) or base ($OCONEt_2$) sensitive phenol protecting groups may be retained by choice. Functionalization of phenethylamines (entry 18), steroids (entries 19, 20), naphthyls (entry 21), phenanthryls (entries 22–24), binaphthyls (entry 25), pyridines (entries 26–29), quinolines (entries 30, 31), and uracils (entries 32, 33) is illustrative of additional scope for this chemistry.

In summary, we have described new Ni(0)-catalyzed aryl carbamate and aryl triflate–Grignard cross-coupling reactions which feature the following: (a) coupling partners that are easily derived from phenols and organic halides and carbamates and triflates which may be readily interconverted; (b) the use of carbamates singularly, and in conjunctive fashion, with directed ortho metalation (1,2-dipole equivalency (4)) providing rapid and regiospecific entries into complex polysubstituted aromatics; (c) the apparent superiority of carbamates and triflates over other phenol derivatives,[6e-g] most of which are incapable of ortho metalation; (d) new methodologies that offer competitive and complementary alternatives to the triflate–aryltin[7b] and triflate–arylboronic acid[7c] regimens. The triflate-based coupling overcomes β-hydride elimination, an oft-observed process of synthetic detriment. The ability to tune in the metal in coupling of aryl triflates with RMgX (Ni) or $RB(OH)_2$ (Pd) derivatives may be of distinctive synthetic value. Further refinement and exploration of these methods is in progress.[11,12]

Note Added in Proof. Since the submission of this paper, a Ni(0) catalyzed vinyl carbamate–Grignard reagent cross-coupling reaction has been brought to our attention: Kocienski, P.; Dixon, N. J. *Synlett* **1989**, *52*. We thank P. S. Bury for this information.

Supplementary Material Available: Experimental procedures and characterization data for new compounds (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(11) All new compounds show analytical and spectral (IR, NMR, MS) data in accord with the given structures.

(12) We are grateful to NSERC Canada and CNPq for financial and scholarship support. We thank Professor G. Queguiner, Rouen, and Dr. J. Muchowski, Syntex, for some starting materials and Professor B. Giese, Universitat Basel, for solitude, support, and space to prepare this manuscript.

A New Channel-Forming Host Macroring. X-ray Crystal Structure of Its Inclusion Compound with DMF

Edwin Weber,*,† Rolf Pollex,† and Matyas Czugler*,‡

Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-5300 Bonn-1, FR-Germany, and Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O. Box 17, H-1025 Budapest, Hungary

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Summary: A macrocyclic host molecule composed of two conformationally inflexible 4,4′-dioxybenzophenone building blocks and two 2,6-methylene-substituted pyridine nuclei is shown to form a crystalline channel structure with included DMF molecules; the unsolvated host compound as a solid is capable of DMF vapor sorption.

Molecular arrangements that are representatives of a channel[1] are in great demand due to their potential behavior as chemical transporter systems[2] or as environments for topochemical reactions.[3] We report here a new mac-

† Universität Bonn.
‡ Central Research Institute for Chemistry, Budapest.

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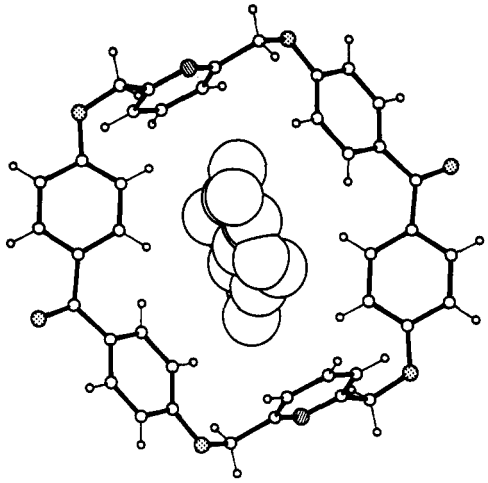
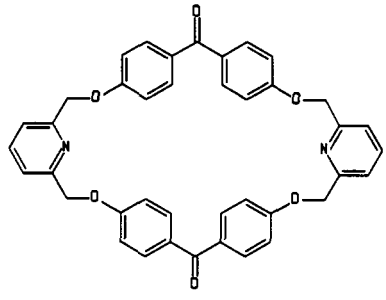


Figure 1. Molecular structure of 1·DMF viewed down nearly perpendicular to the *ac*-plane. C, H and O, N atoms of the host macroring are drawn with 10 and 15% of their respective van der Waals radii, respectively, while the disordered guest model positions are given with 50% of the C van der Waals radius. Insert shows the "bonding" mode of the high electron density peaks for the mean guest molecule.

rocyclic host compound 1 which includes DMF and forms a tubular packing aggregate in the crystalline state which promises future applications.



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The present host molecule 1 is composed of two conformationally inflexible 4,4′-dioxybenzophenone building blocks and two 2,6-methylene-substituted pyridine nuclei connected in such a way that a symmetric structure is formed. Structurally related host macrorings[4] use bis(4-oxyphenyl)methane and analogs as characteristic building units. Force-field (MM2) calculations[5] show the angularly arranged phenylene rings in the bis(4-oxyphenyl)methane unit to be in a pseudo-face-to-face conformation which has been confirmed by structural analyses.[6] In contrast to that, by force field calculations the 4,4′-dioxybenzophenone building block has one of the phenylene rings coplanar to the carbonyl group while the other is inclined (about 55°) relative to this plane. Hence, a very different inside and outside structure of the present host macroring 1 is expected when compared to the known macrocycles.[4]

The macroring 1 (mp 280–282 °C) was synthesized in 26% yield (see supplementary material) via ring closure reaction of 2,6-bis(bromomethyl)pyridine[7] with 4,4′-carbonyldiphenol[8] under high-dilution conditions using Cs_2CO_3 in DMF.[9] Recrystallization from DMF gave the 1:1 inclusion complex with DMF as colorless clear crystals suitable for X-ray structural analysis.[10]

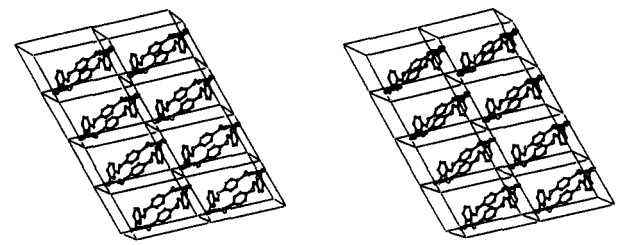

Figure 2. Packing of the host molecules in crystalline 1·DMF (stereo plot) viewed from the *bc*-plane indicating channel structure along the *b*-axis. The disordered guest model (cf. Figure 1) in the center of each macroring is omitted here.

As shown in Figure 1, the host macroring 1 adopts a symmetric conformation with alignment of the aromatic and heteroaromatic groups in alternating almost rectangular (Py/Ph = 82.6 and 84.7°) and 49.5° (Ph/Ph) inclinations with respect to each other, thus offering a spacious shelter. Molecular mechanics calculations (MM2/85) confirm the present ring conformation as being favorable and rather unstrained. There is a significant hole in the macroring of slightly distorted oval shape and suitable dimensions (van der Waals dimensions 4.5 × 6.5 Å) to host a small organic guest, in the present case a molecule of DMF which shows heavy disorder. The guest density is centered near to the middle of the macrocycle at $0,^1/_2,^1/_2$; thus, the "average guest molecule" (Figure 1) sits in the center of the cavity. The steric match of this average density is quite satisfactory on one hand and generous enough on the other to allow for the observed rotational disorder.

These host guest entities, in the same orientation, pack one above the other giving rise to a continuous smooth channel along the *b* direction (Figure 2). The region between the molecular segments of a channel is shielded by the aromatic groups of neighboring channels. Interchannel packing is characteristic of a stacking between pyridine nuclei, which is a typical property of pyridino containing macrorings,[11] and to a certain degree of stacking between any of the phenylene units. Including the molecules of DMF, the packing arrangement may be considered as a solid-state model of a molecular channel with a "frozen state" of guest propagation through the stacked macrorings from one resting place to the next.

Inclusion complexation of the present type is different from the so-called channel clathrates.[12] In these, the channels are created between the host molecules, whereas in the present case they are created mostly within the

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(10) Crystal data for 1·DMF (1:1): $C_{40}H_{30}N_2O_6 \cdot C_3H_7NO$, mol wt = 707.79, triclinic, space group $P\bar{1}$, a = 8.069 (1) Å, b = 9.238 (2) Å, c = 13.471 (1) Å, α = 72.54 (2)°, β = 74.69 (1)°, γ = 74.35 (2)°, Z = 1, D(calcd) = 1.30 g cm^{-3}, crystal size = 0.15 × 0.20 × 0.30 mm. Intensity data were measured at 300(1) K on a Enraf-Nonius CAD4 diffractometer using CuKα (λ = 1.54184 Å) radiation to Θ_{max} = 75°; 3041 unique reflections converged to a final R = 0.077 for 2314 reflections with $I > 3\sigma(I)$; R_w = 0.082 with w = 1 for all observed data. Additional details of the structure solution are given in the supplementary material.
(11) Weber, E. *Synthesis of Macrocycles: The Design of Selective Complexing Agents*; Izatt, R. M.; Christensen, J. J., Eds.; Progress in Macrocyclic Chemistry; Wiley: New York, 1987; Vol. 3, p 337.
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molecules themselves.[13] Based on these results, the 4,4′-dioxybenzophenone unit may be considered a valuable new building block in host design which allows fragmental control of a particular macroring conformation.

Furthermore, we have found that treatment of the present inclusion compound (1·DMF) under reduced pressure (15 Torr) or heating (100 °C) decomposes the complex to yield solid unsolvated 1 which on exposure to vaporos DMF easily resorbes the solvent. Thus compounds of type 1 are promising in chemical sensor development.[14]

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Supplementary Material Available: Experimental procedure for the synthesis of 1 and X-ray data for 1 (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Articles

Preparation of Polyfunctional Allenic Alcohols by the Regioselective Addition of Functionalized Propargylic Chromium(III) Organometallics to Carbonyl Compounds

Kevin Belyk, Michael J. Rozema, and Paul Knochel*,[1]

The Willard H. Dow Laboratories, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

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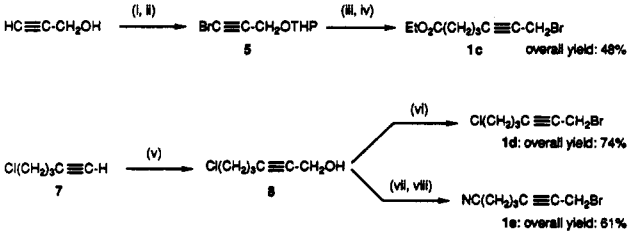
The reaction of propargylic halides 1 (X = Cl, Br) with an aldehyde or ketone (0.67 equiv) in the presence of $CrCl_2$ (2.0 equiv) and LiI (2 equiv, necessary if X = Cl) affords allenic alcohols 3 with excellent regioselectivities (3–6% of the regioisomeric acetylenic alcohol 4 is formed) and in good yields (68–90%). Interestingly, this method allows the generation of highly functionalized intermediate propargylic chromium organometallics contained an ester, cyano, or chloride functionality. The α-alkyl-substituted propargylic bromide 10 reacts with benzaldehyde yielding the acetylenic alcohol 11 as a diastereomeric mixture of only one regioisomer (90% yield).

Propargylic and allenic organometallics of magnesium,[2a–c] zinc,[2d–i] aluminum,[2j–l] silicon, or tin[3] and boron[4] react with aldehydes with variable regioselectivity[2–4] affording a mixture of homopropargylic and allenic alcohols.

Scheme I[a]



[a] Key: (i) DHP (1.5 equiv), TsOH cat., CH_2Cl_2, 5 °C, 2 h, 88%; (ii) (a) BuLi (1.0 equiv.), Et_2O, −78 to −60 °C, 0.5 h; (b) Br_2 (1.0 equiv), Et_2O, −78 °C, 1 h, 81%; (iii) $EtO_2C(CH_2)_3Cu(CN)ZnI$ (1.3 equiv), THF, −78 to −40 °C, 2.5 h, 74%; (iv) PPh_3Br_2 (2.2 equiv), CH_2Cl_2, 5 °C, 1.5 h, 70%; (v) (a) BuLi (1.0 equiv), ether, −78 to −60 °C, 0.5 h; (b) $(CH_2O)_n$ (excess), ether, 35 °C, 2 h, 88%; (vi) PBr_3 (0.36 equiv), ether, −20 to 5 °C, 2 h, 84%; (vii) NaI (1.5 equiv), KCN (2.5 equiv), DMSO, 50 °C, 12 h, 90%; (viii) PBr_3 (0.36 equiv), ether, −20 to 20 °C, 2 h, 78%.

Furthermore, the presence of functional groups such as esters or nitriles is not tolerated in these organometallics.[5] Gorè showed that *unfunctionalized* propargylic halides

(1) Present address: Philipps-Universitat Marburg, Fachbereich Chemie, Hans-Meerwein-Strasse, D-3550 Marburg, Germany.

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(5) The treatment of ethyl 7-bromo-5-heptynoate 1c with zinc in THF leads to an intermediate propargylic reagent which attacks the ester carbonyl group.

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