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Functionalizations of [6]- and [7]Helicenes at Their Most Sterically Hindered Positions

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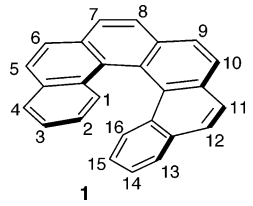
Although the reactions of enol ethers of aryl methyl ketones with benzoquinone make it easy to prepare nonracemic helicenes that are substituted by hydroxyl groups at their 1,ω-positions, the hydroxyl groups fail to facilitate the introduction of electrophiles ortho to them. However, ethers of [6]- and [7]helicenols prepared in this way, seemingly because of the activation by the alkoxyl groups at the 6-positions, combine with electrophilic reagents to introduce bromines and acyl groups exactly into these positions. Moreover, these bromine and acyl groups can be transformed into other functional groups (including phosphine oxides and acetylenes), the ether functions adjacent to these functional groups can then be removed, and the phenols can be oxidized to quinone-acetals. An alternative way to introduce functional groups next to the phenols is to rearrange their phosphate esters. Two reactions that differentiate the ends of the helicenes are also described.

Introduction

Helicenes, examples of which are [6]- and [7]helicenes, structures **1** and **2**, are chiral, conjugated molecules whose derivatives in enantiomerically pure form have been used as building blocks for helical conjugated polymers,[1] helical ligands,[2] and structures that exhibit unusual chiro-optical,[3] electro-optical,[4] and fluorescense[5] properties or act as catalysts for enantioselective transformations,[6,7] as chiral derivatizing agents,[8] as enantioselective complexing agents,[9] as chiral auxiliaries,[10] as inducers of enantioselectivity,[11] or as fluoresence sensors.[12] These examples usually have substituents in positions 1,2 and 15,16 of a [6]helicene skeleton, positions 1,2 and 17,18 of a [7]helicene skeleton, or positions 1,2 and ω,(ω−1) of a general helicene.



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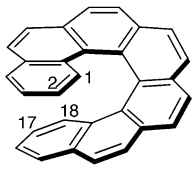

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The way helicenes substituted at positions 1 and 2 were prepared originally was by photocyclizing appropriately substituted diarylethenes.[13] [6]- and [7]Helicenes bearing OMe,[10b,13b,14] Br,[9a,11a,13a,15] CHO,[13a] CO_2R,[13a,16] CN,[11a,13a] and Me[13a,17] were synthesized in this way. However, this photochemical route has significant defi-

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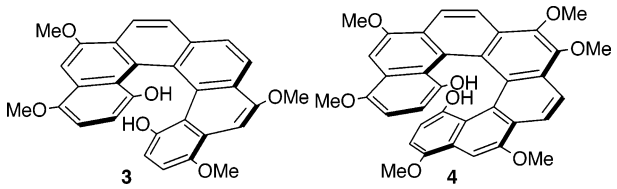
ciencies. It requires high dilution, which seriously limits the amount of the material that can be prepared, and it does not tolerate some groups (notably NO_2 and NH_2).[13a] Among more recently developed methods to synthesize functionalized helicenes,[18] the Diels−Alder reaction of enol ethers of bis(aryl methyl ketones) with 1,4-benzoquinone has been used to prepare substantial amounts of helicenebisquinones.[19] In both the photochemical and Diels−Alder methods, the functional groups are usually introduced before the main aromatic backbone is constructed. Functionalization of unsubstituted 1- or 2-positions *after* the main skeleton has been built is rare. Examples are the addition of nucleophiles, amines,[19a,20] and bromide[1d] to 6,11-dialkoxy[6]helicene-1,4,13,16-bisquinone, which regioselectively give, after oxidation, the bisquinone's 2,15-dibromo- and 2,15-diamino-derivatives.

In this paper, we describe how electrophiles can be introduced with high regioselectivity onto methoxylated [6]- and [7]helicenes that have been made by the Diels−Alder-based route. Bromination, formylation, and acetylation substitute positions 2 and 15 in the former and the analogous positions, 2 and 17, in the latter. The methoxyl groups adjacent to the acetyl groups can then be cleaved selectively by the action of BBr_3. The resulting helical salicylaldehydes and helical *o*-hydroxyacetophenones are similar to helical salicylaldehydes previously used to synthesize helical conjugated ladder polymers.[1d] The functional groups introduced are transformed into others. The regioselectivities of the transformations are confirmed by X-ray analysis.

Results

Optically active dihydroxyhelicenes **3** and **4** were used for the studies because they are particularly easy to prepare.[19d,21] The reasons are that the Russig−Laatsch reaction specifically alkylates those hydroxyl groups of [6]- and [7]helicenebishydroquinones[19d,21] that are at the peripheries, leaving the other hydroxyl groups of the hydroquinones at the 1- and ω-positions, and that these helicenols are especially easy to resolve.[3a,22] The absolute stereochemistries of **3** and **4** are also known.[19d,22] The isomers that are dextrorotatory at the wavelength of the sodium D-line have the *P* configuration. Although it would seem that hydroxyl groups at the 1- and ω-positions could be used as handles to install additional functionality at the 2- and 15-positions of the [6]helicene and the 2- and 17-positions of the [7]helicene, attempts to brominate **3** and **4** regioselectively[1d] gave complex mixtures. Attempts to rearrange their diacetates by the Fries procedure, using $AlCl_3$ or $Sc(OTf)_3$, to formylate the diols by the Duff procedure (hexamethylenetetramine and TFA),[23] or to hydroxymethylate the diols by the use of paraformaldehyde and either HCl alone or HCl in AcOH led only to decomposition products. Instead of introducing formyl groups next to the hydroxyl groups, both $POCl_3$ in DMF and the Arnold−Vilsmeier reagent[24] in DMF gave mixtures whose main components (up to 40%) were the products that have formyl groups next to only one of the hydroxyl groups and in place of the hydrogen of the other hydroxyl group. But as shown in Scheme 1, the 2- and (ω−1)-positions could successfully be functionalized in **3a** and **4a**, the ethers formed when **3** and **4** are methylated.



Bromination of **3a** and **4a** with 2 equiv of NBS in 2:1 $CH_3CN-CH_2Cl_2$[25] gave dibromohelicenes **3b** and **4b** in high yields without detectable traces of regioisomers. (NBS (1 equiv) gave **3b** or **4b**, along with the monobrominated products and starting materials **3a** or **4a**, in ca. 1:2:1 ratios.) Similarly, the benzyl ethers of **3** and of **4** gave the corresponding dibromo derivatives in 93% and 96% yields (see below), but the yields of the dibromo derivatives obtained from other ethers and esters were lower.[26] Formylation of **3a** and **4a** in DMF at 25−80 °C with (chloromethylene)dimethylammonium chloride (the Arnold reagent)[23] gave only monoformylated helicenes **3c** and **4c**. No diformylated helicenes were obtained. Moreover, even for monoformylation to succeed with **3a**, the temperature had to be raised to 50 °C. However, when the reagent was DMF plus $POCl_3$ and the temperature was 50−70 °C, the diformylations succeeded, and the

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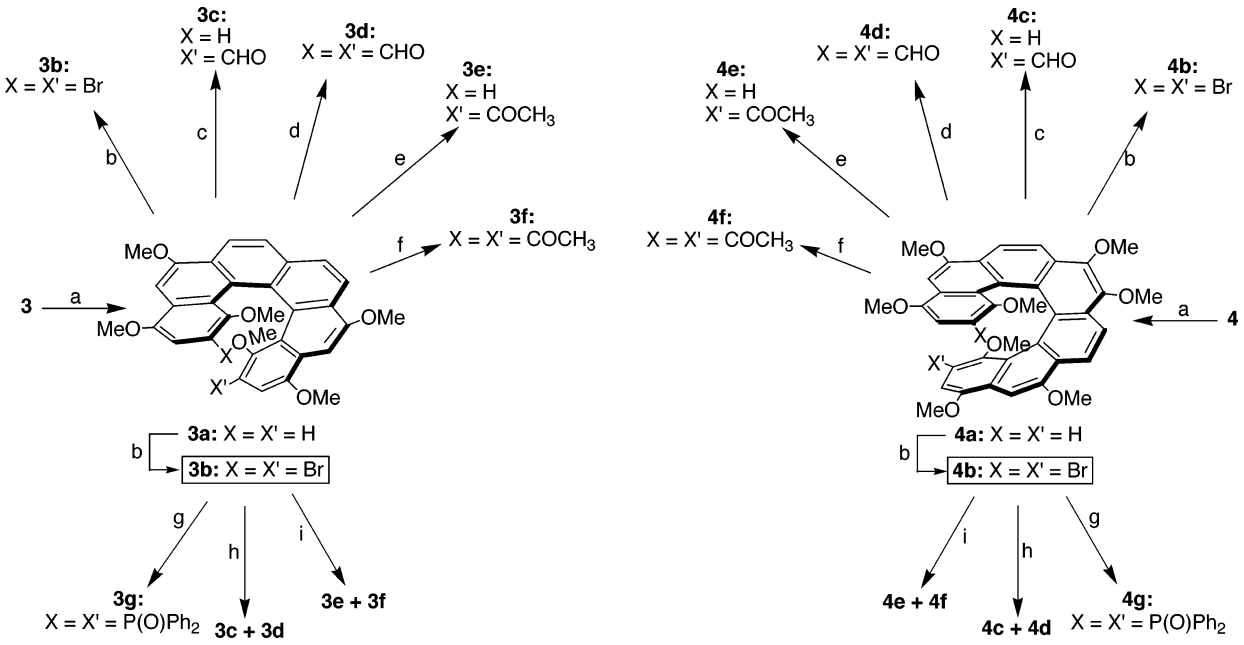
(26) The bis-TMS and bismethoxymethyl ethers of **2** gave yields of 10% and <10%, while the bispivalate of **2** gave a 28% yield.

SCHEME 1[a]



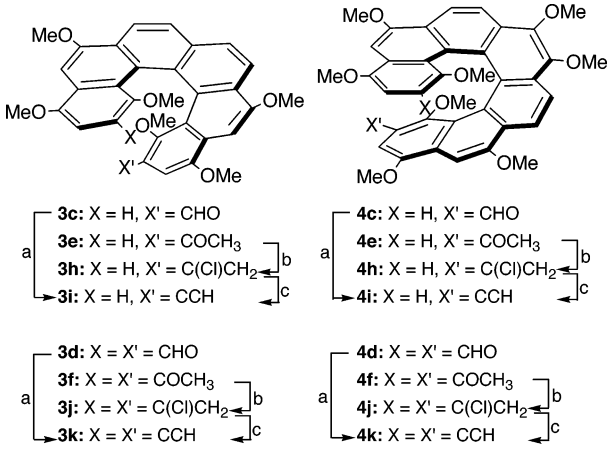
[a] Reaction conditions and yields. (a) *t*-BuOK, THF, then MeI (yields: **3a**, 91%; **4a**, 91%). (b) NBS, CH_3CN, CH_2Cl_2, 25 °C, 1 h (yields: **3b**, 93%; **4b**, 87%). (c) $ClCH{=}NMe_2Cl$, DMF, and$(CH_2Cl)_2$ (for **3c**) or CH_2Cl_2 (for **4c**) (yields: **3c**, 59%; **4c**, 60%). (d) DMF, $POCl_3$, CH_2Cl_2, 50−70 °C (yields: **3d**, 61%; **4d**, 87%). (e) AcCl, $AlCl_3$, CH_2Cl_2, 0 °C (yields: **3e**, 80%; **4e**, 53%); or Ac_2O, $AlCl_3$, CH_2Cl_2, 0 °C (yield: **4e**, 63%). (f) $AlCl_3$, AcCl, CH_2Cl_2, 25 °C (yields: **3f**, 83%; **4f**, 80%). (g) (i) BuLi; (ii) $Ph_2P(O)Cl$, −78 °C, 4 h (yields: **3g**, 51%; **4g**, 67%). (h) BuLi, THF, −78 °C, then DMF (yields: **3c**, 35%, and **3d**, 59%; **4c**, 54%, and **4d**, 21%). (i) BuLi, THF, −78 °C, then *N*-methoxy-*N*-methylacetamide (yields: **3e**, 37%, and **3f**, 17%; **4e**, 24%, and **4f**, 9%).

bisaldehydes **3d** and **4d** could be obtained in 61% and 87% yields. The structure of **4d** was confirmed by X-ray diffraction analysis.

Acetyl groups could also be introduced. Friedel−Crafts acetylation with $AlCl_3$ and AcCl in CH_2Cl_2 converts **3a** and **4a** at 0 °C into monoacetylated helicenes **3e** and **4e** and at 25 °C into the diacetylated products **3f** and **4f**. A slightly better yield of **4e** (63% instead of 53%) was obtained when Ac_2O was used instead of AcCl. The regioselectivities of bromination, formylation, and acetylation are all the same. This was shown by the dibrominated helicenes **3b** and **4b** when treated with BuLi and then DMF, giving the diformylated helicenes **3d** and **4d**. Monoformylated **3c** and **4c** were side products of these transformations. Similar transformations of **3b** and **4b** with *N*-methoxy-*N*-methylacetamide[27] gave, respectively, mixtures of **3e** plus **3f** and **4e** plus **4f**.

Other functional groups could be placed in the 2- and (ω−1)-positions by transforming those introduced initially. One functional group introduced in this way was the ethynyl group, which was studied because ethynyl functions at positions 2 and 15 made it possible to convert a [6]helicene into a helical oligomer and a helical cyclophane.[28] Initial attempts to convert monoaldehyde **4c** into its 1,1-dibromoethylene derivative by the action of CBr_4 and PPh_3[29] were indeed successful, but attempts to convert this derivative into alkyne **4i** gave only low yields

SCHEME 2[a]



[a] Reaction conditions and yields. (a) (i) $ClCH_2PPh_3^+$ Cl^-, $LiN(Si(CH_3)_3)_2$, THF; (ii) MeLi, THF (yields over the two steps: **3i**, 72%; **3k**, 56%; **4i**, 76%; **4k**, 53%). (b) PCl_3, PCl_5, PhH (yields: **3h**, 56%; **4h**, 64%; **3j**, 56%; **4j**, 43%). (c) LDA, THF, −78 °C to +25 °C (yields: **3i**, 82%; **4i**, 80%; **3k**, 97%; **4k**, 74%).

(ca. 30% for the two steps). Treatment of bisaldehyde **3d** with dimethyl-1-diazo-2-oxopropylphosphonate, as described by Bestmann et al.,[30] also produced the corresponding bisalkyne **3k** in very poor yield (traces according to TLC). However, **3k**, as well as alkynes **3i**, **4i**, and **4k**, could be obtained in moderate to good yields (Scheme 2, paths a) by treating the aldehydes with (chloromethyl)-triphenylphosphonium chloride plus lithium bis(trimeth-

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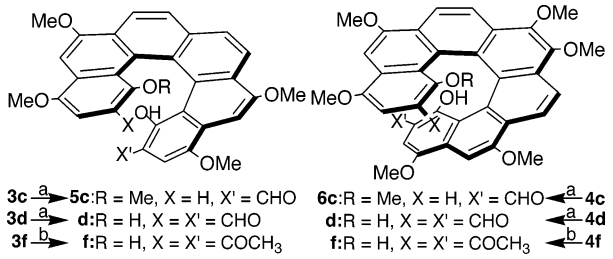
SCHEME 3[a]



[a] Reaction conditions and yields. (a) BBr_3, tetrabutylammonium iodide, CH_2Cl_2, −78 °C to 25 °C (yields: **5c**, 37%; **6c**, 66%; **5d**, 58%; **6d**, 47%). (b) BBr_3, CH_2Cl_2, −78 °C to 25 °C (yields: **5f**, 89%; **6f**, 75%).

ylsilyl)amide[27] and by treating the resulting mixtures of isomeric vinyl chlorides[31] with MeLi.

As shown in Scheme 2, the ethynyl-substituted helicenes **3i**, **3k**, **4i**, and **4k** can also be prepared by dehydrohalogenating the vinyl chlorides, formed by treating the corresponding acetyl derivatives (**3e**, **3f**, **4e**, and **4f**) with PCl_3 and then PCl_5 (Scheme 2, paths b and c).[32,33] The structure of **4i** was demonstrated by X-ray diffraction analysis.

Other functional group transformations could be used to introduce phosphorus-containing functions next to the oxygens at positions 1 and ω. Thus, combining **3b** and **4b** with BuLi followed by $ClP(O)Ph_2$ (or alternatively, and in similar yields, with $ClPPh_2$ followed by H_2O_2) gave **3g** and **4g**, respectively, accompanied by minor amounts of monophosphine oxides.

To install reactive sites at the 1,ω-positions, in addition to those at the 2- and (ω−1)-positions, one approach was to regioselectively cleave the 1,ω-methoxy groups of **3f** and **4f**. Treatments with $AlCl_3$ in CH_2Cl_2[34] returned the starting materials, and those with BCl_3[35] gave complex mixtures. However, the action of BBr_3 in CH_2Cl_2 achieved the desired result (Scheme 3).[36] For the procedure to succeed with the aldehyde derivatives **3c**, **3d**, **4c**, and **4d**, tetrabutylammonium iodide had to be added to the reaction mixture.[37] (Otherwise the starting materials were returned.)[38] The salicylaldehydes **5c**, **5d**, **6c**, and **6d** were then obtained in 37−66% yields. That structures **6c**, **5f**, and **6f** were assigned correctly was verified by X-ray diffraction analysis. For the analysis of compound **6f**, a highly disordered cocrystallized molecule of ethyl acetate was treated as a diffuse contribution by the SQUEEZE method.[39] The X-ray data corrected by SQUEEZE showed 200 electrons per unit cell, close to the required value of 192 electrons per unit cell.

Attempts were also made to cleave the methoxy groups adjacent to the phosphine oxide functions in **3g** and **4g** by means of BBr_3 (without Bu_4NI), but the yields were less than 15%. However, the goal of preparing **7f** and **8f** could be achieved by making use of the selectivity with which benzyl ethers are cleaved. Thus (Scheme 4) debenzylation by hydrogen in the presence of 10% palladium on carbon reduces **7b** in ethyl acetate to **7c** in a yield of 81% and **8b** in ethyl acetate to **8c** in a yield of 85%. It is also interesting that further reaction can be used to give **7d** and **8d**. The hydrogen pressure is increased from 2.5 to 4 atm, and the reaction time is extended from 30 min to 6−10 h. The consequence is that **7d** and **8d**, molecules that are selectively functionalized at one end, can be obtained easily and in good yields.

The benzyl groups could also be removed from the ether functions of phosphine oxides **7e** and **8e** (themselves prepared in the same way as the methyl ethers **3g** and **4g** in Scheme 1), but not, as above, by means of hydrogen, but rather by means of ammonium formate and palladium on carbon.[40] Dihydroxybisphosphines **7g** and **8g** could then be prepared in excellent yields by removing the oxides from the phosphorus atoms of the resulting **7f** and **8f** with $HSiCl_3$ plus Bu_3N,[41] and they were found to be fairly stable to oxidation. ^1H NMR analysis indicated that after its solution in $CDCl_3$ had been open to the air for 24 h, the extent to which **8g** had oxidized to the monophosphine oxide was 20%. The pure solid did not oxidize appreciably during a period of 3 days.

A strategically different way to selectively functionalize helicenes at the 1,ω- and 2,(ω−1)-positions made use of 1,3 migrations (Scheme 5).[42] Upon treatment with LDA, diethyl phosphates **9** and **10** rearrange cleanly, regiospecifically, and in good yields to **11** and **12**.

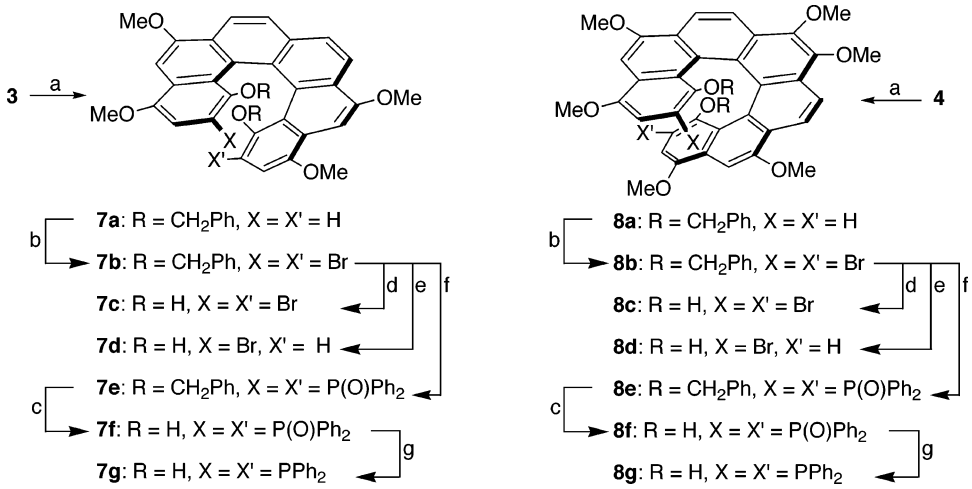
Also studied was whether functionalized helicenes could be prepared by transforming the 1,ω-diols in the molecules synthesized here into other functional groups, in particular into quinone-acetals. Indeed, as Scheme 6 shows, $PhI(O_2CCF_3)_2$ oxidizes **7c**, giving **13** in 58% yield, and **8c**, giving **14** in 55% yield.[43] The major byproducts are the bromohelicene quinones, probably formed by hydrolysis of the acetals. However, while this I^{III} reagent fails to oxidize **5f** and **6f** to the corresponding quinone-acetals, **15** and **16**, $Tl(NO_3)_3 \cdot 3H_2O$ in $HC(OMe)_3$ solvent does, in yields of 97% and 94%.[44]

Discussion

Electrophilic bromination, formylation, and acetylation introduce substituents exclusively at positions 2 and 15 of **3** and at the corresponding positions of **4** (2 and 17), even though these positions are more sterically hindered than those on the peripheries of the rings. This regioselectivity, which probably is a consequence of the electron-donating effect of the alkoxy groups at positions 6,[45] is

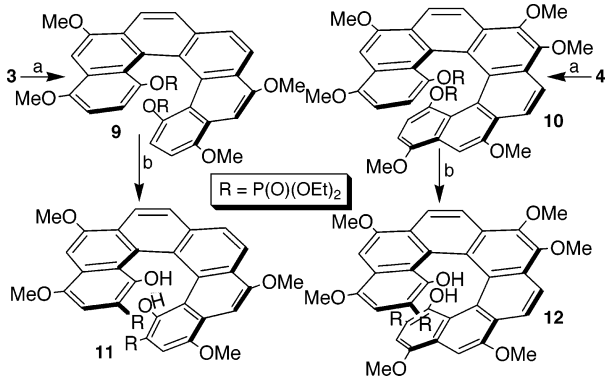
(31) The isomers were not separated.
(32) This procedure, developed for electron-rich aromatic compounds, is that of: Evans, K. L.; Prince, P.; Huang, E. T.; Boss, K. R.; Gandour, R. D. *Tetrahedron Lett.* **1990**, *47*, 6753.
(33) For an example of a procedure used previously, see: Buckle, D. R.; Rockell, C. J. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2443.
(34) Parker, K. A.; Petraitis, J. J. *Tetrahedron Lett.* **1981**, *22*, 397.
(35) Miyaura, N. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 1, p 648.
(36) Nagaoka, H.; Schmid, G.; Iio, H.; Kishi, Y. *Tetrahedron Lett.* **1981**, *22*, 899.
(37) For a similar method, using BBr_3, NaI, and 15-crown-5, see: Niwa, H.; Hida, T.; Yamada, K. *Tetrahedron Lett.* **1981**, *22*, 4239.
(38) Other reagents ($BeCl_2$, LiCl, PhSeNa, $PhCH_2SeNa$, Ph_2PLi, and PhSNa) also either failed or gave complex mixtures.
(39) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, 194.
(40) Martinborough, E.; Denti, T. M.; Castero, P. P.; Wyman, T. B.; Knobler, C. B.; Diederich, F. *Helv. Chim. Acta.* **1995**, *78*, 1037.
(41) Wang, Y.; Xin, L.; Ding, K. *Tetrahedron. Lett.* **2001**, *43*, 159.
(42) Dhawan, B.; Redmore, D. *J. Org. Chem.* **1991**, *56*, 833.
(43) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *J. Org. Chem.* **1987**, *52*, 3928.
(44) (a) McKillop, A.; Perry, D. H.; Edwards, M.; Antus, S.; Farkas, L.; Nogradi, M.; Taylor, E. C. *J. Org. Chem.* **1976**, *41*, 282. (b) Horie, T.; Yamada, T.; Kawamura, Y.; Tsukayama, M.; Kuramoto, M. *J. Org. Chem.* **1992**, *57*, 1038.

SCHEME 4[a]



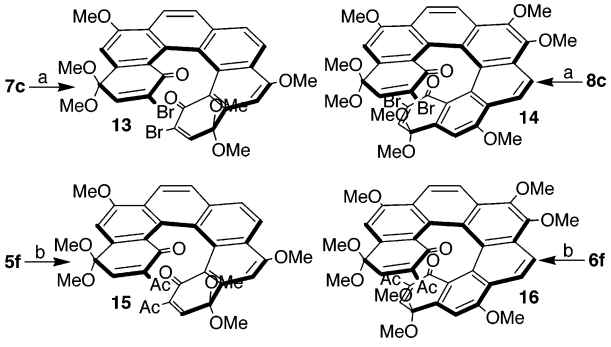
[a] Reaction conditions and yields. (a) NaH, DMF, then $PHCH_2Br$, 10 h (yields: **7a**, 85%; **8a**, 82%). (b) NBS, CH_3CN, CH_2Cl_2, 25 °C, 1 h (yields: **7b**, 93%; **8b**, 96%). (c) HCO_2NH_4, 10% Pd/C, THF, MeOH, 8−10 h (yields: **7f**, 83%; **8f**, 85%). (d) For **7c**: 10% Pd/C, $P(H_2) = 4$ atm, EtOAc, 5 h (yield: 81%); for **8c**: 10% Pd/C, $P(H_2) = 2.5$ atm, EtOAc, 30 min (yield: 85%). (e) 10% Pd/C, $P(H_2) = 4$ atm, EtOAc, 10 h for **7d** (yield: 57%) and 6 h for **8d** (yield: 64%). (f) BuLi, THF, −78°C, 40 min, then $ClP(O)Ph_2$, −78 °C to +25 °C, 10 h (yields: **7e**, 71%; **8e**, 62%). (g) $HSiCl_3$, Bu_3N, toluene, reflux, 20 h (yields: **7g**, 95%, **8g**, 91%).

SCHEME 5[a]



[a] Reaction conditions and yields. (a) NaH, THF, 30 min, then $ClP(O)(OEt)_2$, 25 °C, 8 h (yields: **9**, 87%; **10**, 91%). (b) LDA, THF, −55 °C to +25 °C, 4 h (yields: **11**, 100%; **12**, 98%).

SCHEME 6[a]



[a] Reaction conditions and yields. (a) $PhI(O_2CCF_3)_2$, K_2CO_3, CH_3CN, CH_3OH, 25 °C, 20 min (yields: **13**, 58%; **14**, 55%). (b) $Tl(NO_3)_3 \cdot 3H_2O$, $HC(OCH_3)_3$, CH_3OH, CH_2Cl_2, −30 °C to −10°C, 1 h (yields: **15**, 97%; **16**, 94%).

unlike that found in the reactions of unsubstituted [6]-helicene. In the latter, bromination takes place at positions 5 and 12 and acetylation and nitration at positions 5 and 8.[46] However, there is no doubt about the regiospecificities, for the X-ray analyses of **4d**, **4i**, **5f**, **6c**, and **6f** prove the structures of the acetylation and formylation products, as well as those of the products of the ether cleavages. Moreover, since the products of the brominations were converted into those of formylation and acetylation, all three electrophilic substitutions are regioselective in the same sense. The transformations in Scheme 6 provide a novel way for a functional group (the carbonyl group) that differs from other functional groups in the molecule to be introduced specifically at the 1- and ω-positions.

The ability to functionalize helicenes inside the helical structures is important because helicenes functionalized in this way display the useful properties enumerated in the Introduction. Moreover it is these positions that should be, and experimentally seem to be, most sensitive to the chirality of the helicene ring system. Thus, a series of experiments showed both that principle and why camphanoyloxy groups at the 1- and ω-positions of helicenes, but not on their peripheries, allow such molecules to be resolved.[19d,21,22]

Noteworthy is that only three steps are required to convert **3** into **5c** (in 20% yield), into **5d** (in 25% yield), or into **5f** (in 67% yield) and **4** into **6c** (in 36% yield), into **6d** (in 37% yield), or into **6f** (in 55% yield). The precursors, nonracemic **3** and **4**, are themselves prepared from racemic helicenebisquinones in three steps and in ca. 70−72% yields.[19d,21] In contrast, the synthesis of the only analogue of these compounds (a [6]helicene with salicylaldehyde rings at both ends) required eight steps

(45) Similar effects are seen in Friedel−Crafts acylations of 1,2,4,5,8-pentamethoxynaphthalene ((a) de Koning, C. B.; Giles, R. G. F.; Engelhardt, L. M.; White, A. L. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3209) and of 2-methoxynaphthalene ((b) Girdler, R. B.; Gore, P. H.; Hoskins, J. A. *J. Chem. Soc.* (*C*) **1966**, 181. (c) Pivsa-Art, S.; Okuro, K.; Miura, M.; Murata, S.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1703. (d) Kobayashi, S.; Komoto, I. *Tetrahedron* **2000**, *556*, 6463).

(46) op den Brouw, P. M.; Laarhoven, W. H. *Recl.: J. R. Neth. Chem. Soc.* **1978**, *97*, 265.

from a racemic helicenebisquinone,[1d,19a] the overall yield was only 12%, and the method was not extended to [7]-helicene derivatives. The conversions of **3** into **7b** and **4** into **8b** also require only three steps, and the latter transformation has given 14 g at a time with ease. These substances are useful because the bromine substituents can easily be transformed into other functionalities and the ether functions subsequently removed, again easily. The preparations of **11** and **12** are even shorter; only two steps are required from **3** and **4**, and the overall yields are excellent. The quantitative yields of the [6]- and [7]-helicenes in the base-promoted 1,3-migrations are notably large when compared to the yields (ca. 39−95%) in similar reactions of benzene and naphthalene derivatives.[42,47]

Also significant are that **3a** and **4a** can be monoformylated and monoacetylated selectively, not just diformylated and diacetylated, and that one of the two bromine groups in **7b** and **8b** can be removed selectively. These are significant because the reaction of benzoquinone with the enol ethers of bisdiacetylaromatics constructs four rings at a time, providing helicenes very efficiently, but the helicenes it gives are identically substituted at their two ends. For the two ends to be differentiated, there are only two ways to proceed. One is to carry out a synthesis that does not take advantage of geminate constructions.[6c] The other is to differentiate the two ends after the helicene's ring system is prepared. What is remarkable about the acylation experiments described above is that electrophilic substitution can be controlled adequately by a substituent deactivating a ring five or six away. While such control cannot be achieved in brominations (at least not in the experiments with *N*-bromosuccinamide described above), it can be, as Scheme 1 shows, in reactions that introduce acyl substituents, formyl groups (paths c and d), and acetyl groups (paths e and f). And while the brominations could not be controlled to introduce only one bromine per molecule, Scheme 4 shows that it was possible to remove selectively one of the two that were introduced.

(47) Dhawan, B.; Redmore, D. *J. Org. Chem.* **1984**, *49*, 4018.

Conclusion

Nonracemic dihydroxyhelicenes **3** and **4**, which are conveniently prepared on a large scale, can serve as precursors of helicenes that are substituted by a variety of fuctional groups at positions 1,2 and 15,16 of [6]-helicene and the corresponding 1,2- and 17,18-positions of [7]helicene, despite the steric hindrance at these positions. Moreover, it is possible to introduce acyl or bromine groups selectively at either one or both of the 2- and 15-positions of the [6]helicene and at the corresponding 2- and 18-positions of the [7]helicene. The monosubstitutions make it possible to synthesize well-functionalized helicenes efficiently by a process that builds both ends simultaneously and yet allows the ends to be differentiated.

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Supporting Information Available: Experimental details; ^{1}H, ^{13}C NMR, IR, CD, and UV spectra for compounds **3a**−**3k**, **4a**−**4k**, **5c**, **5d**, **5f**, **6c**, **6d**, and **6f**; ^{1}H, ^{13}C NMR, and IR spectra for compounds **7a**−**g**, **8a**−**g**, **9**, and **11**−**16**; and X-ray diffraction data for (±)-**4d**, (*M*)-(−)-**4i**, (±)-**5f**, (±)-**6c**, and (±)-**6f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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