Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Katz, Thomas J. , Sudhakar, Anantha , Yang, Bingwei and Nowick, James S.(1989) 'Synthesis of Conjugated Optically Active Polymetallocenes', Journal of Macromolecular Science, Part A, 26: 2, 309 — 326

To link to this Article: DOI: 10.1080/00222338908051976

URL: http://dx.doi.org/10.1080/00222338908051976

J. MACROMOL. SCI.–CHEM., A26(2&3), pp. 309-326 (1989)

SYNTHESIS OF CONJUGATED OPTICALLY ACTIVE POLYMETALLOCENES

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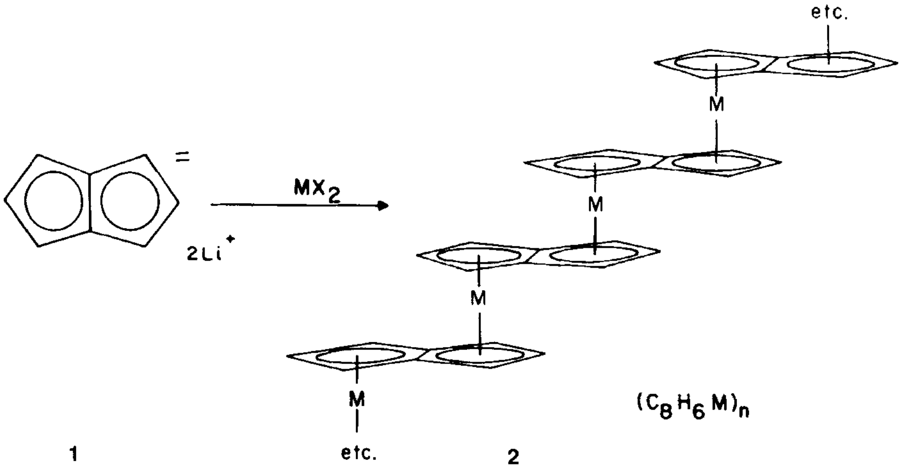
ABSTRACT

The development of methodology for synthesizing new materials in which metal atoms are linked by hydrocarbons whose electronic conjugation is unbroken is described. The fundamental idea is to twist the hydrocarbons into helices. By attaching bulky groups to their precursors, the helices can be made to twist mainly in one direction. The molecules synthesized are helicenes capped by five-membered rings to which metals are attached. If the size of the helix is chosen appropriately, a polymeric structure forms in which hydrocarbon rings and metal atoms alternate. An oligomer with Structure **22** is the first such material prepared. It and related structures might be precursors of molecular solenoids, examples of which are not yet known.

INTRODUCTION

The synthesis of the pentalene dianion **1** many years ago [1] suggested that its combination with transition metal halides might yield new structures, **2**, in which hydrocarbon rings and metal atoms alternate. Such materials might exhibit high thermal stability (because every bond other than the C–H's, which are inherently strong, should be multiple), and they might exhibit interesting



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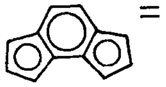
conductive properties as well, for if some of the metal atoms were oxidized from the +2 to the +3 oxidation state, the conjugated system of electrons might delocalize the electron vacancy from one metal to the next. To study these possibilities, the pentalene dianion was combined with a variety of transition metal salts, two of which, cobalt and nickel, gave characterizable materials $(C_8H_6M)_n$, where M is the metal [2]. Unfortunately, *n* was equal to two; the materials were only dimers.

The *as*-indacene dianion **3** was also prepared to see whether it would give larger polymers, but like pentalene dianion, it too gave only dimers **4**, those prepared having M = Fe, Co^+, and Ni [3]. These were the first examples of structures in which two metals were sandwiched between a pair of planar



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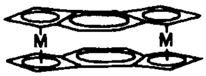

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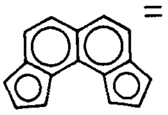

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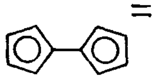

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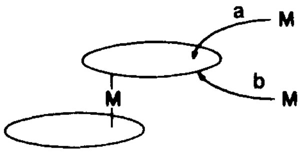
hydrocarbons—structures that in the United States would be recognized as "hero sandwiches." Others have been prepared by combining metal salts and related dianions, like **5** [4] and **6** [5], or by bridging molecules of ferrocene [6].

One view of the difficulty that causes **1** and **3** to give only dimers is that the metals, instead of bonding to opposite faces of one ring system as in *a* (Structure 7), bond to the same face as in *b*, suggesting that the undesired



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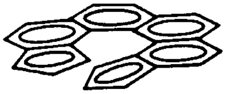

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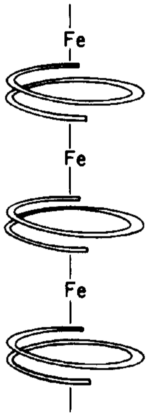

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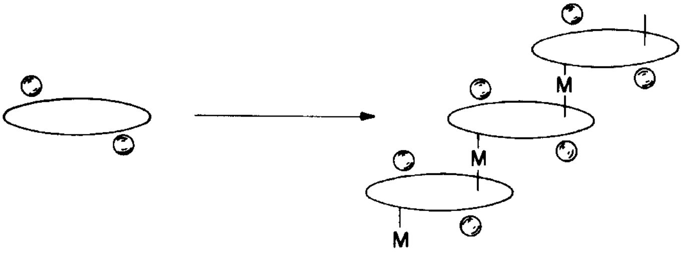
approach is blocked. One way to achieve this would be to float encumbering groups as in Eq. (1) above the conjugated hydrocarbon plane on the left and below it on the right, for these groups would ward off the metal, and a way to float the blocking groups would be, as in Eq. (2), to distort the ring system into a helix, a structure in which the ring at one end is indeed blocked at the top and



(1)

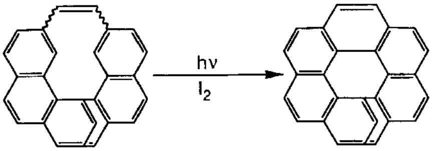
at the other is blocked at the bottom. An example of a chemical representation is Structure **8**. This is a helicene capped at both ends by unsaturated five-membered rings. It should, with transition metal halides (e.g., ferrous chloride), give helical polymers, represented as Structure **9**. Although not planar, the helix's pitch should attenuate the overlap of adjacent *p*-orbitals by only a miniscule amount, and oxidation should then allow electrons to delocalize throughout.

(2)

A prominent feature of this structure is its chirality. If the hydrocarbon used to prepare it were one of the optically pure antipodes, an electron tanslating from one metal atom to the next would twist, and always in the same direction. The material would be a molecular solenoid. Its optical, magnetic, and conductive properties should be unique.

SYNTHESIS OF A HELICAL METALLOCENE

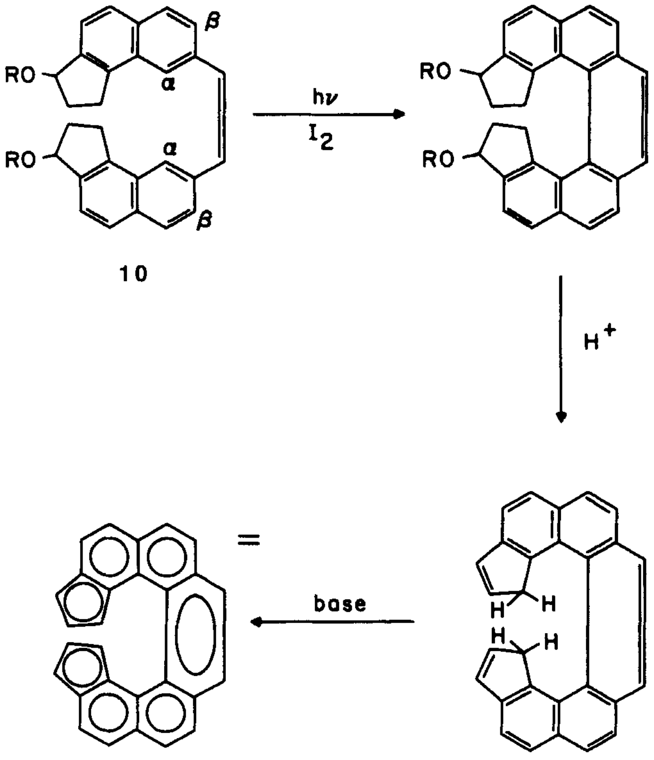
To synthesize such structures it should be possible to follow paths Martin and Laarhoven cleared to reach helicenes comprised purely of benzene rings **8** [7], the key step being the photocyclization developed by Mallory of a stilbene to a phenanthrene [8]. Equation (3) illustrates this. What is required appears to be methodology to 1) to fuse five-membered rings to the ends of the helicene, so that valencies are available to bond to the metals, and 2) to drive the photocyclization to forge a bond between α-positions rather than between α and β, as when **10** is cyclized (Eq. 4), so that the structure formed is helical. The disquieting possibility, despite the precedents of Martin and Laarhoven, is that the clutter of saturated five-membered rings might hinder α-positions from uniting, forcing the photocyclization to give a nonhelical structure in which α- and β-carbons are bonded. The fact is that the cyclization does proceed according to Eq. (4), implying that the electronic preference favoring α-positions prevails [9].



(3)

Because the two end rings in Structure **11** essentially superimpose, it is not surprising that its dianion (prepared from **11** and *n*-butyllithium) with ferrous chloride gives a helical ferrocene (**12**, Eq. 5) in which iron has inserted between the end rings of one molecule [10]. The structures of this material, as well as that of **11**, have been determined by x-ray crystallography, and among the interesting features is the flexibility of the accordion shape, for the angle between the normals to the two end rings can be made to vary enormously [11]. In the hydrocarbon it is 69.1° (to accommodate the methylene hydrogen poking toward an opposed benzene ring, and in the ferrocene it is only 19.4° (to accommodate the iron-carbon bond length).

The idea that a helical structure would prevent dimers like **4** from forming

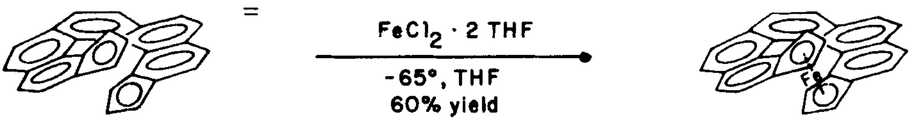


10

11

(4)

is correct, but it has not led, as was originally supposed, to a polymer. It gave rise instead to a monomer! However, the preparation of this monomer clarifies the actions that have to be taken for analogous syntheses to give the desired helical polymers. One is to incorporate into the helix either one or more extra benzene rings, or possibly one fewer, because, while the end rings in **11** are on top of one another where a metal can span them, they cannot be in homologs. Another is to make the helix, which in the synthesis in Eq. (4) is obtained racemic, optically active.



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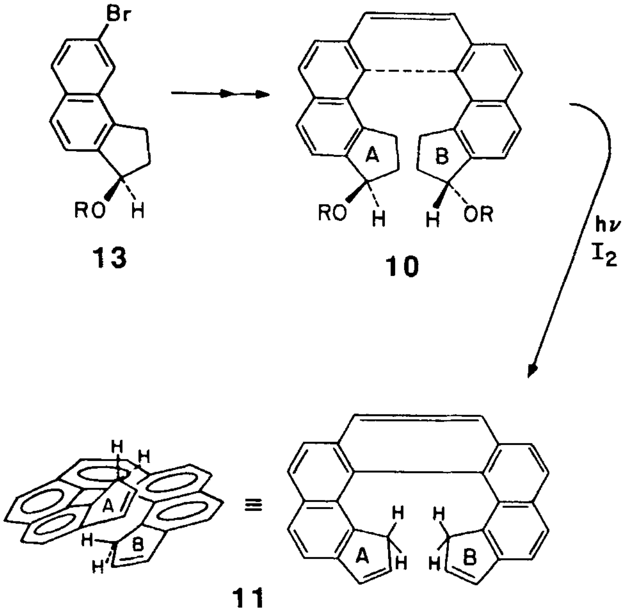
(5)

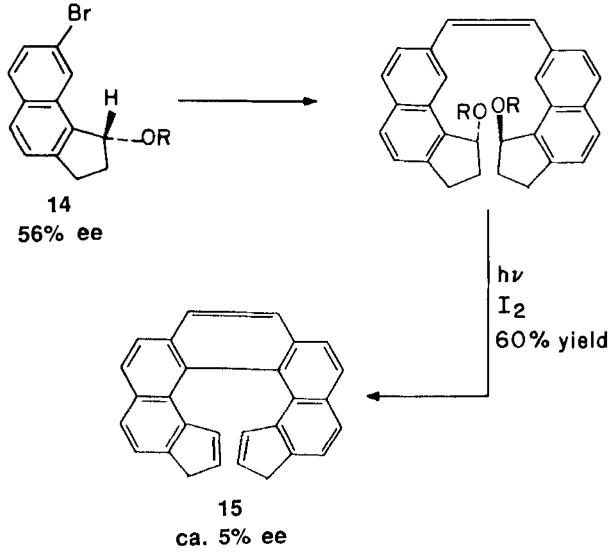
INDUCING HELICES TO WIND IN ONE DIRECTION

Consider the idea summarized in Scheme 1, which describes what might happen if the starting material **13** used to synthesize **10** were optically active [12]. Even though the ether function defining the only center of asymmetry in this structure is eliminated when **11** is formed, it might be expected to control the direction in which the helix winds during the photocyclization. That is because, if the –OR function is "up" in **13**, in **10** it must be "up" in the ring at the left and "down" in the ring at the right. Since the stereochemistry of the helix is determined by whether the photocyclization places Ring A over Ring B or Ring B over Ring A, and since only the latter causes the –OR groups to clash, avoidance of this steric problem should result in the former mode: the helix should wind to the right.

The fact is that, when the idea was tested experimentally, it failed completely. The bromoether **13** was synthesized, in which the levorotatory enantiomer was present in 40% enantiomeric excess, but the photocyclization of the optically active stilbene **10** prepared from it gave helicene **11** that was racemic (enantiomeric excess (ee) <3%).



SCHEME 1.



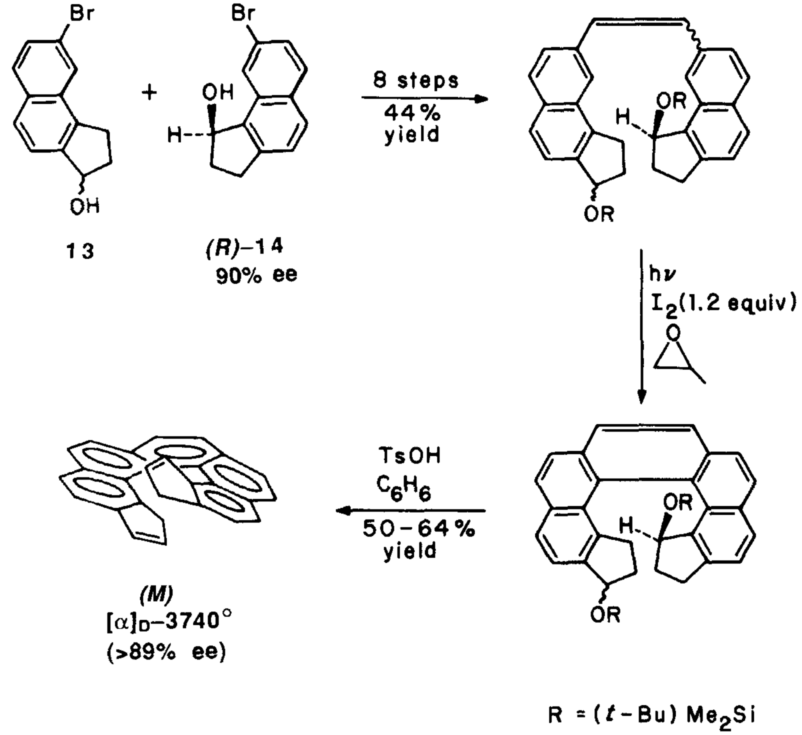
14
56% ee

15
ca. 5% ee

SCHEME 2.

Because the idea seemed worth pursuing nonetheless, and because it seemed possible that the steric interaction supposed to give rise to asymmetric winding would be amplified if the directing alkoxyl groups were not on the outside carbon of the five-membered rings, but rather on the more-congested inside carbon, Isomer **14** of bromoether **13** was synthesized, optically active, and the experiment summarized in Scheme 2 was carried out. However, although this procedure gives the helical hydrocarbon (a double-bond isomer of **11**)—its structure was also analyzed by x-ray diffraction by Ian Williams at MIT—the scheme shows that the optical activity was lost.

The problem seems to be that the ether functions, which are supposed to direct the helix winding, are being eliminated by the photochemically generated hydrogen iodide prior to the photocyclization. Excess propylene oxide was therefore added to the photocyclization reaction mixture, and, as expected, it appears to scavenge the HI, but the optically active helix does not form. Indeed, no helical structure could be isolated, implying that such structures form only if the ether functions have been eliminated before they can exert their directive effect. This would mean that using an alkoxyl group to control the direction in which a helix winds could not work.



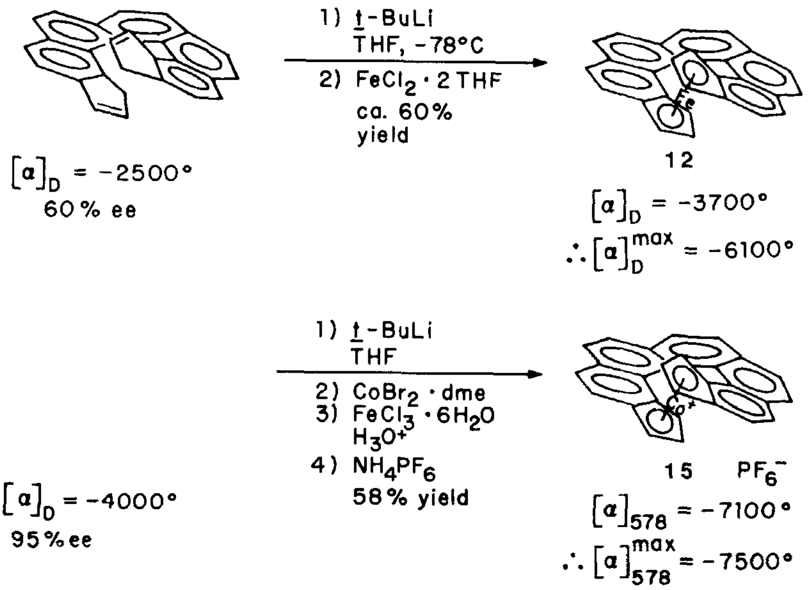
SCHEME 3.

However, the hypothesis that an alkoxyl group on the inside can control the helicity and that a scavenger of HI is required to prevent its elimination suggests one more version of the fundamental experiment, and as Scheme 3 shows, it is successful [13]. The enantiomeric excess induced is superb, and the direction of winding is exactly that expected. When the right half has the *R*-configuration, the five-membered ring on the right is placed over that on the left. This is known because the absolute configurations of **14** and of the helical hydrocarbon it gives are known. It is also remarkable that *only* the inside alkoxyl determines the direction of ring winding; the outside alkoxyl has no effect on the helicity. When combined with the same enantiomer of **14**, both the *S*- and *R*-enantiomers of **13** give the *same* helical hydrocarbon. This is fortunate for three reasons. It means that only **14** has to be prepared optically active (**13** can be racemic), and **14**, it turns out, is much easier than **13** to obtain in high enantiomeric excess. Moreover, since the synthesis of the stilbene requires more steps for one part of the molecule than for the other, the lengthier synthesis can be carried out with the more available racemic half.

Equation (6) summarizes the general point in a schematic way. A single appropriately placed "knob," avoiding steric interactions with the rest of a ring system, can cause a helix to wind specifically in the direction that keeps the knob outside. The knob can then be cut off.

(6)

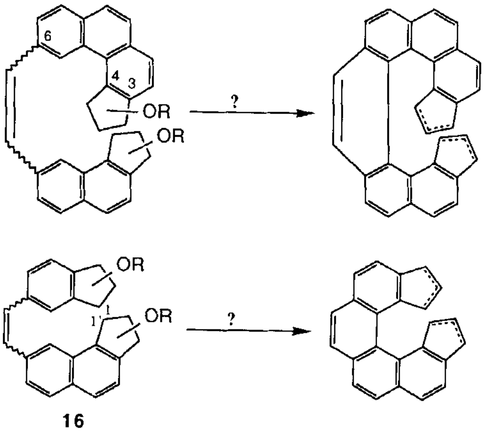
With the helical hydrocarbon in hand, it is simple to prepare ferrocene **12** as well as the related cobaltocenium salt, **15**, in optically active form (Scheme 4) [12].



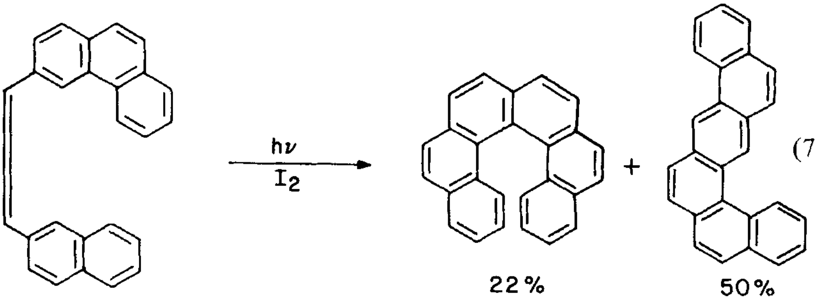
SCHEME 4.

SYNTHESIS OF A NINE-RING HELICENE-METAL OLIGOMER

To obtain helicenes that would give polymers because they cannot give monomers—that is, helicenes with more rings between the terminal five-membered rings (or possibly one fewer)—it would be ineffective to add or subtract the additional rings to or from those at the ends of the ethylene as suggested in Scheme 5. Suppose a ring were added. The molecule from which the saturated carbons have been removed gives only a small amount of helical product (Eq.7) [14] and the steric encumbrance of these carbons added in Scheme 5 (their hydrogens poke up and down) should diminish the fraction of helical product further, possibly to zero. Worse yet, this hypothesis would be diffi-



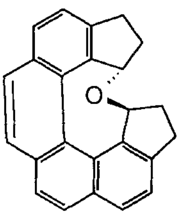
SCHEME 5.



(7)

cult to test, for phenanthrenes substituted at Positions 3, 4, and 6 are not easily prepared.

Suppose a ring were removed. A major feature would be the absence of electronic effects to direct photocyclizations to α-positions in naphthalenes [9, 14, 15]. One test of this approach, carried out by photoirradiating Structure **16** with methoxyls at the 1 and 1′ positions, does give a helicene. Its structure, analyzed by mass spectrometry, ^{1}H-NMR spectroscopy, and x-ray diffraction (this last by Dr. Ian Williams at MIT), is the pleasing one displayed as **17**, but there are two problems: the yield is only 5%, presumably in large part because electronic directive effects are lacking, and the ether function eluded attempts to eliminate it.



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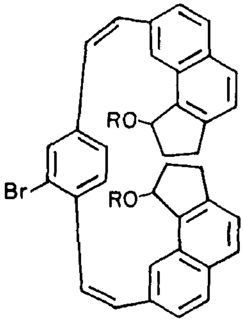

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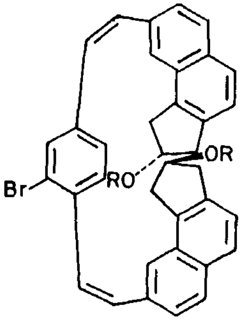

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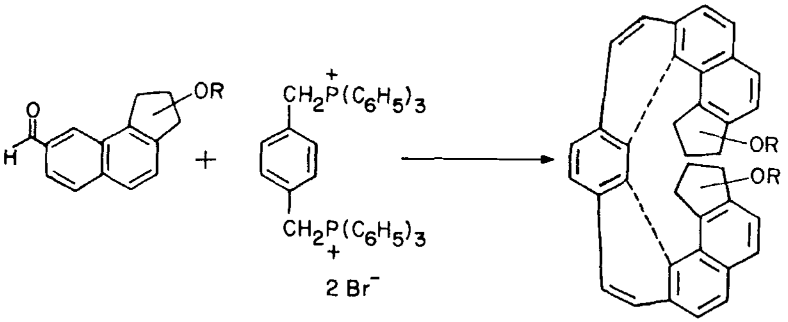
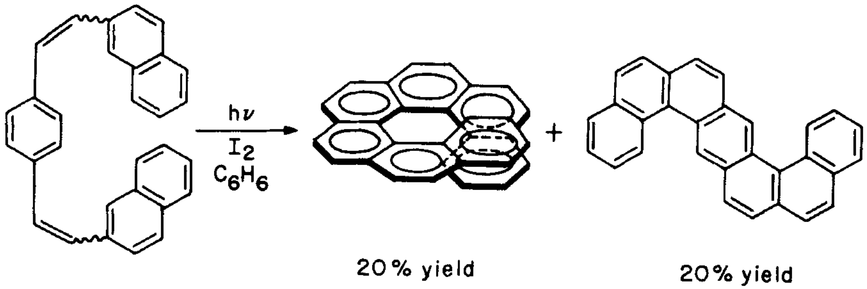
An alternative to the first approach in Scheme 5 is displayed in Eq. (8). It circumvents the problem of phenanthrene synthesis by using the cyclopentanonaphthalenes already synthesized, and it uses only one other building block, a bis-phosphonium salt that is easy to obtain. However, this approach

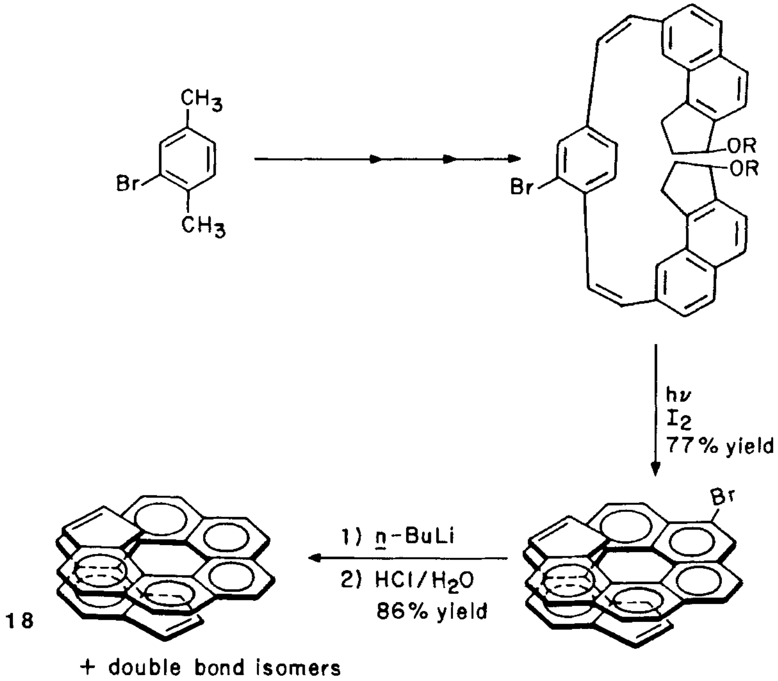


(8)



(9)

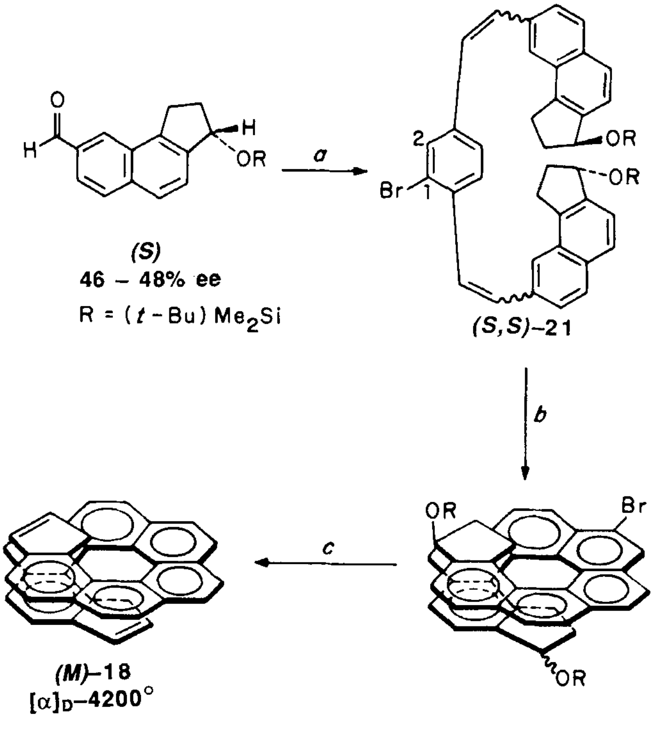
is unlikely to succeed (indeed, when tested it failed), for, as Eq. (9) shows, the analog without the five-membered rings gives the helicene in only 20% yield [16], a figure that should be diminished greatly by the steric effects of the added five-membered rings.



SCHEME 6.

It turns out that there is a simple solution to this problem (Scheme 6), for a single bromine substituent in the precursor bis-phosphonium salt, which is prepared easily from 2-bromo-*p*-xylene, directs the photocyclization to give the nine-ring helicene in which the caps are five-membered and from which the bromine is easily removed [13]. (This directive effect of bromine could also be applied to Eq. (9), greatly improving the synthesis of the parent [7]-helicene [17].)

It only remained to obtain the ring system optically active and to incorporate the metal. Experiments to direct the winding of the helix were therefore carried out with **19**, but no helical product was recognized after photoirradiation. Structure **20** was therefore prepared and tried instead. It gave the optically active helicene, but the alkoxyls, now not in the benzylic positions, could not be eliminated. Finally, experiments were carried out with **21**, and as Scheme 7 shows, these give helicene **18** that is optically active. The scheme incorporates three principles clarified by the early stages of the work: that

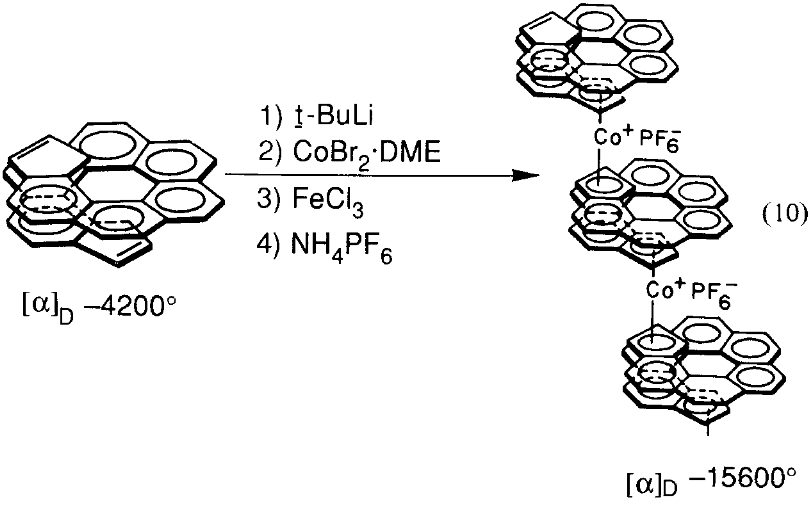


SCHEME 7. ^{a}1,4-bis[$Ph_3P^+CH_2$]-2-BrC_6H_3 $2Br^-$/LiOEt. ^{b}$h\nu$, PhH, I_2, propylene oxide. ^{c}(1) *t*-BuLi/THF; (2) *p*-TsOH, PhH.

the asymmetry of carbon can be translated into asymmetry of ring winding that propylene oxide present during photocyclization prevents the directing alkoxyls from being eliminated by acid, and that bromine directs the photoreaction to give the helix.

The optically active helicene **18** when combined with *t*-butyllithium and then with ferrous chloride would be anticipated to give Structure **9**, an optically active helical ferrocene polymer. Instead, however, a brown, uncharacterizable product was obtained, resembling those arising when the parent bis-indenyliron decomposes, seemingly as a result of air oxidation [18].

However, bis-indenylcobaltocenium ion, like other cobalt analogs of ferrocene—that is, cobaltocenium salts—is much less sensitive to oxidation than the iron derivative [19]. Accordingly, the experiment was repeated (Eq. 10) with cobalt bromide in place of ferrous chloride, and after oxidation with ferric chloride, ammonium hexafluorophosphate precipitated an oligomeric cobaltocenium salt, **22**, a beautiful red material [13].



(10)

22

Reasons for believing it to have Structure **22** [13] include the ^{13}C-NMR spectrum exhibiting not only peaks characteristic of aromatic carbons but also those distinctive of cobaltocenium ions, and the positions of these peaks (~ 96, 75, and 80 ppm) being remarkably similar to those of the cyclopentadienyl resonances in diindenylcobalt(III). However, in the helicene derivative these carbons are, compared to those in diindenylcobalt(III), shielded by

TABLE 1. Comparison of Molar Ellipticities ([Θ]) and Rotational Strengths (**R**) of Related Absorptions[a]

		[Θ]	**R**		[Θ]	**R**
Structure	λ_{max}, nm	cgs units		λ_{max}, nm	cgs units	
22	263	3.32×10^{6}	3.58×10^{-37}	474	-8.44×10^{5}	-1.21×10^{-37}
15	243	5.51×10^{5}	?[b]	478	-1.17×10^{5}	-1.45×10^{-37}
Ratio		6.0	–		7.2	8.3
18	285	1.70×10^{5}	8.80×10^{-39}			
11	282	7.55×10^{5}	5.60×10^{-38}			
Ratio		0.23	0.16			

[a] Calculated for samples with enantiomeric excesses of 100%. The samples of **11**, **18**, and **22** had enantiomeric excesses of 60%. The sample of **15** had an enantiomeric excess of 95%.

[b] The peak appears to be broadened by one that overlaps it.

an extra 2-3 ppm, approximately the amount added to the shielding of a benzene carbon when it is placed over another in a helicene. The elemental analyses correspond to ~3.13 [9] helicene units and 2.13 cobalts, and therefore a number-average molecular weight of about 1900. In accord with this, the fast atom bombardment mass spectrum shows as the only prominent peaks at high mass those corresponding to four nine-membered rings (144 carbons) and three cobalts, three nine-membered rings and two cobalts, and two nine-membered rings and one cobalt.

The oligomer exhibits very high optical activity: at 100% enantiomeric excess $[\alpha]_D = -26{,}000°$. More telling is the comparison in Table 1 of the molar ellipticities and rotational strengths of the oligomer **22** and the monomer **15**. The values are about 7 times larger for the oligomeric cobaltocenium salt than for the monomeric one, even though the ratios for the corresponding hydrocarbons are more nearly 1/6. They imply that the rotational strength increases with the number of units in the oligomer, and suggest that the optical activity of larger polymers could be enormous.

CONCLUSIONS

The research summarized above shows how a structure can be synthesized whose mobile electrons are conjugated from one end to the other, constrained to a helical path of specific handedness, and bonded to two similar structures by links that preserve electron mobility. It should be possible to use the procedures summarized here to synthesize other examples that are larger, with only partially filled valence levels. These could be the first of a class of truly novel materials.

ACKNOWLEDGMENTS

We are grateful to Dr. Ian Williams for his x-ray diffraction analysis of the structure of **17**, to Dr. Mark Teasley for helpful discussion, and to the national Science Foundation and the National Institutes of Health for support under Grants DMR-82-13794 and 5-R01-GM34737.

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