perature, a complex mixture of isomers is initially produced. Upon being allowed to stand, however, the mixture slowly isomerizes (2 days) to the thermodynamically more stable, diequatorial adduct, **29**. Oxidation of **29** with ozone (-78 °C), followed by regiospecific elimination in refluxing CH_2Cl_2, yields **22**,[4b] which is conveniently hydrolyzed to octalone **23** in refluxing 90% formic acid.[10]

A more subtle application of this enone transposition sequence involves the conversion of certain chiral 5-substituted cyclohexenones into their optical antipodes. Thus, by performing the sequence of reactions indicated in Scheme I, (-)-**24** is converted to (+)-**24** in at least 92% optical purity.

On examination of Scheme I, it is important to realize that each of these transpositions can be accomplished by using just two or three flasks, with little or no purification of intermediates being necessary. Moreover, even in its current, nonoptimized state, we are able to use this methodology to effect both simple and alkylative 1,3-enone transpositions on a variety of structurally diverse enones in approximately 40-60% overall yields. Further studies involving the synthetic and mechanistic aspects of this work are currently in progress and will be the subject of future reports.

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Registry No. 6, 1896-62-4; **7**, 36004-04-3; **8**, 73587-62-9; **9**, 73587-63-0; **10**, 35845-66-0; **11**, 78-94-4; **12**, 115-18-4; **13**, 62493-31-6; **14**, 107-86-8; **15**, 73587-64-1; **16**, 73587-65-2; **17**, 73587-66-3; **18**, 73587-67-4; **19**, 73587-68-5; **20**, 73587-69-6; **21**, 73587-70-9; **22**, 73587-71-0; **23**, 22844-34-4; (-)-**24**, 54307-74-3; (+)-**24**, 15466-88-3; **25**, 73610-84-1; **26**, 73610-85-2; **27**, 73587-72-1; **28**, 73587-73-2; **29**, 73587-74-3; PhSeCl, 5707-04-0.

Supplementary Material Available: Experimental Section describing details of a representative 1,3-enone transposition sequence (**15** → **19**) (3 pages). Ordering information is given on any current masthead page.

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(10) Lansbury, P. T. *Acc. Chem. Res.* **1972**, *5*, 311.

(11) Fellow of the Alfred P. Sloan Foundation, 1980-1984.

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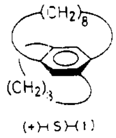
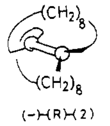
Synthesis of a C_3-Symmetric Tris-Bridged [2.2.2]Cyclophane with a Triphenylmethyl Component

Summary: High-dilution coupling of **6** and **7** afforded the trithia derivative **8** which was converted, via the trisulfone **9**, into 17-methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (**10**) with C_3 symmetry.

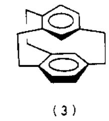
Sir: We have been interested in gyrochiral twisted π-electron systems, and the preparations and chiroptical properties of (+)-(*S*)-[8.8]paracyclophane (**1**)[1] (D_2 symmetry) and (-)-(*R*)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**2**)[2] (D_2 symmetry) were reported from our laboratory. An extension of our recent study on the twisted [2.2.2] tris-bridged cyclophane derivative **3**[3] with C_2 symmetry led us to investigate a novel [2.2.2] tris-bridged cyclophane system (**10**, Scheme I) with C_3 symmetry which is composed of the mesitylene and the *m*-substituted triphenylmethane components, and this communication describes its preparation as well as its conformational mobility.



(+)-(S)-(1)

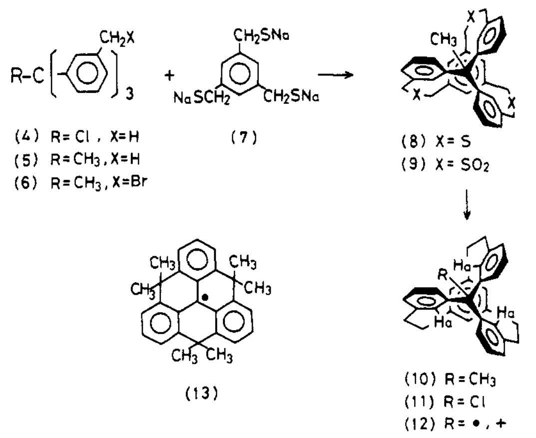


(-)-(R)-(2)



(3)

Scheme I



The Grignard reaction of the *m*-substituted triphenylmethyl chloride **4**[4] with methylmagnesium iodide afforded the higher homologue **5** (mp 73-74 °C, 82% yield) whose NBS photobromination in CCl_4 gave a 41% yield of the tribromide **6**, mp 111-112 °C. High-dilution coupling of **6** and the sodium salt of 1,3,5-tris(mercaptomethyl)benzene (**7**) was carried out in a benzene-ethanol (1:1) solution, and the product was purified through SiO_2 column chromatography to provide the trithia derivative **8**[5] (17% yield), melting at 220-221 °C after recrystallization from ethyl acetate. The trisulfone **9** (mp >350 °C), secured from **8** by conventional hydroperoxide oxidation with a quantitative yield, was vacuum sublimed (0.1 mmHg) and slowly passed through an evacuated Pyrex pyrolysis tube heated at 540 °C. Column chromatography (SiO_2) of the product followed by recrystallization from hexane gave a 55% yield of 17-methyl[2.2.2](1,3,5)benzeno(3,3′,3″)triphenylmethanophane (**10**):[6] mp 213-214 °C, UV (isooctane) λ_{max} nm (log ε) 223 sh (4.49), 256 sh (2.94), 263 (2.99), 271 sh (2.69). Anal. Found: C, 92.70; H, 7.26.

Inspection of a molecular model reveals that **10** has a chiral strain-free rigid conformation with C_3 symmetry which can convert into the enantiomer via various labile

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(1) (a) Synthesis of the racemic modification: M. Nakazaki, K. Yamamoto, and S. Tanaka, *Tetrahedron Lett.*, 341 (1971); M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Org. Chem.*, **41**, 4081 (1976). (b) Preparation of the optically active modification and chiroptical properties: M. Nakazaki, K. Yamamoto, and M. Itho, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki and K. Yamamoto, *Chem. Lett.*, 1051 (1974); M. Nakazaki, K. Yamamoto, M. Itho, and S. Tanaka, *J. Org. Chem.*, **42**, 3468 (1977).

(2) (a) Synthesis of the racemic modification: M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Chem. Soc., Chem. Commun.*, 346 (1977); M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Am. Chem. Soc.*, **101**, 147 (1979). (b) A paper on asymmetric synthesis and chiroptical properties is to be submitted for publication.

(3) M. Nakazaki, K. Yamamoto, and Y. Miura, *J. Chem. Soc., Chem. Commun.*, 206 (1977); M. Nakazaki, K. Yamamoto, and Y. Miura, *J. Org. Chem.*, **43**, 1041 (1978).

(4) J. H. Brown and C. S. Marrel, *J. Am. Chem. Soc.*, **59**, 1175 (1937).

(5) Satisfactory spectroscopic data and elemental or exact mass analyses were obtained for all new compounds.

(6) Following the nomenclature proposed by Vogtle: F. Vogtle and P. Neumann, *Tetrahedron*, **26**, 5847 (1970); F. Vogtle and G. Hohner, *Angew. Chem., Int. Ed. Engl.*, **14**, 497 (1975).

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conformations with C_1 symmetry, and this is supported by its temperature-dependent NMR spectra. The NMR signals at −10 °C were readily assigned: δ 2.22 (3 H, s, CH_3), 2.3–3.3 (12 H, m, CH_2), 5.05 (3 H, d, J = 2 Hz, Ar H_a), 6.37 (3 H, s, mesitylene Ar H), 6.8–7.1 (9 H, m, Ar H). Two aromatic protons are outstanding; the observed meta coupling (J = 2 Hz) and the fairly shielded nature assigned the three hydrogens at δ 5.05 to the H_a of the triphenylmethane component which pointed to the inside of the cage structure, and the other three-hydrogen aromatic signal centered at δ 6.37 was assigned to the protons of the mesitylene component which suffered a mild shielding from three outer benzene rings. At 40 °C, the original complex multiplet of the methylene protons coalesced to broad peaks at δ 2.8 and 3.1 (3:1 integrated areas) which further coalesced into a broad singlet centered at δ 2.72 at 60 °C, reflecting rather rapid conformational conversion.

Presently, we are engaged in the synthesis of the chloride **11** which would generate the cation or radical **12** which, possessing the central sp^2 carbon atom of triphenylmethyl group at a bridgehead position, should make an interesting counterpart of **13**[7] which has the sp^2 center coplanar with the outer benzene rings.

Registry No. 4, 73635-66-2; **5**, 73635-67-3; **6**, 73635-68-4; **7**, 63877-73-6; **8**, 73663-55-5; **9**, 73651-36-2; **10**, 73651-37-3.

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[7] F. A. Neugebauer, D. Hellwinkel, and G. Aulmich, *Tetrahedron Lett.*, 4871 (1978).

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