(A) to a substituted bicyclo[2.1.0]pent-2-ene (I)[11] is followed by a 1,3-sigmatropic shift (B) to II, in which aromaticity has been restored.[12] This intermediate then opens (C) to the isoindene system (III);[13] a [1,5] sigmatropic shift of hydrogen (D), in either of two possible directions, restores aromaticity and gives the rearranged indene isomers.[14,15]

The overall rearrangement is the first example of a photochemically induced reorganization of the indene carbon skeleton.[17]

Acknowledgment. Support of this work by the U.S. Army Research Office (Durham) and a Standard Oil of Ohio Fellowship to Fred Palensky, is gratefully acknowledged.

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(3) (a) J. J. McCullough and M. R. McClory, *J. Am. Chem. Soc.*, **96**, 1962 (1974); (b) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); (c) J. J. McCullough and A. J. Yarwood, *J. Chem. Soc., Chem. Commun.*, 485 (1975).

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(5) The indenes and their photoproducts are known compounds and were prepared by literature procedures.

(6) Monitored by analytical GLC at 100 °C using a 150 ft × 0.01 in. UCON LB-550 X coated Golay column.

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(8) Determined by examination of the intensity of UV absorption at 398 nm.

(9) These represent the first such spectral observations for a non-phenyl-substituted isoindene at room temperature. See also: W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. V. Horak, Abstracts of the 173rd National Meeting of the American Chemical Society, March 21–25, 1977, New Orleans, La., Abstracts, ORGN 83. These workers report an alternate synthesis of 2,2-dimethylisoindene at room temperature, its photochemical conversion to 5,5-dimethylbenzobicyclo[2.1.0]pent-2-ene, and the thermal reversion of this reaction.

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(15) (a) Conversion of the indene to II may also be viewed as a di-π-methane rearrangement,[16] though by contrast with the usual circumstance, the two π systems are conjugated. (b) The increased efficiency, upon alkylation of the 1 and 2 positions, may be a result of the expected stabilization of the cyclopropane moiety in I; the inhibition by a 3-alkyl substituent is not readily rationalized, though a steric inhibition of step B is conceivable.

(16) For a review of the di-π-methane rearrangement, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

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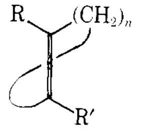
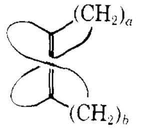
[10.10]Betweenanene: the First Known Member of a Novel Class of Fused Bicyclic Trans Cycloalkenes

Sir:

It has long been recognized that cycloalkenes are capable of cis–trans isomerism.[1] *trans*-Cyclooctene (I, $n = 6$, R = R′ = H) is the smallest isolable member of the trans cycloalkene family, while *trans*-cycloheptene (I, $n = 5$, R = R′ = H) and *trans*-cyclohexene (I, $n = 4$, R = R′ = H) have both been proposed as fleeting intermediates.[2,3] Interactions between the double bond and proximate centers on the spanning carbon chain account for many of the interesting properties of this family, particularly in the smaller members. Chemically, the so-called transannular reactions most strikingly illustrate the consequences of such proximity.[4] Physical phenomena include (1) the chirality and optical stability of *trans*-cyclooctene and (presumably) 1,2-disubstituted trans cycloalkenes (e.g., I, $n = 8$, R = CH_3, R′ = CH_2OH)[6] resulting from steric barriers to rotation of double bond substituents past the carbon chain and (2) the observed dipole moment of *trans*-cyclooctene caused by out of plane bending and rehybridization of the strained π bond.[7]



I



II

For some time now we have been interested in developing a route to a novel and heretofore unknown class of bicyclic trans cycloalkenes wherein the two rings share a common double bond. This class of chiral olefins which we have designated [*a.b*]betweenanenes (II)[8] promises to show unusual chemical and physical properties as a consequence of the aforementioned features of trans cycloalkenes and the buried nature of the double bond, especially in the smaller ring members. We intend to study and report on such matters in due course. Our work to date has been directed toward unequivocal synthetic schemes for producing these compounds. Herein we describe the synthesis of [10.10]betweenanene (**13t**), the first known member of the family, along with its cis isomer, bicyclo[10.10.0]docos-1(12)-ene (**13c**), by a structurally definitive route.

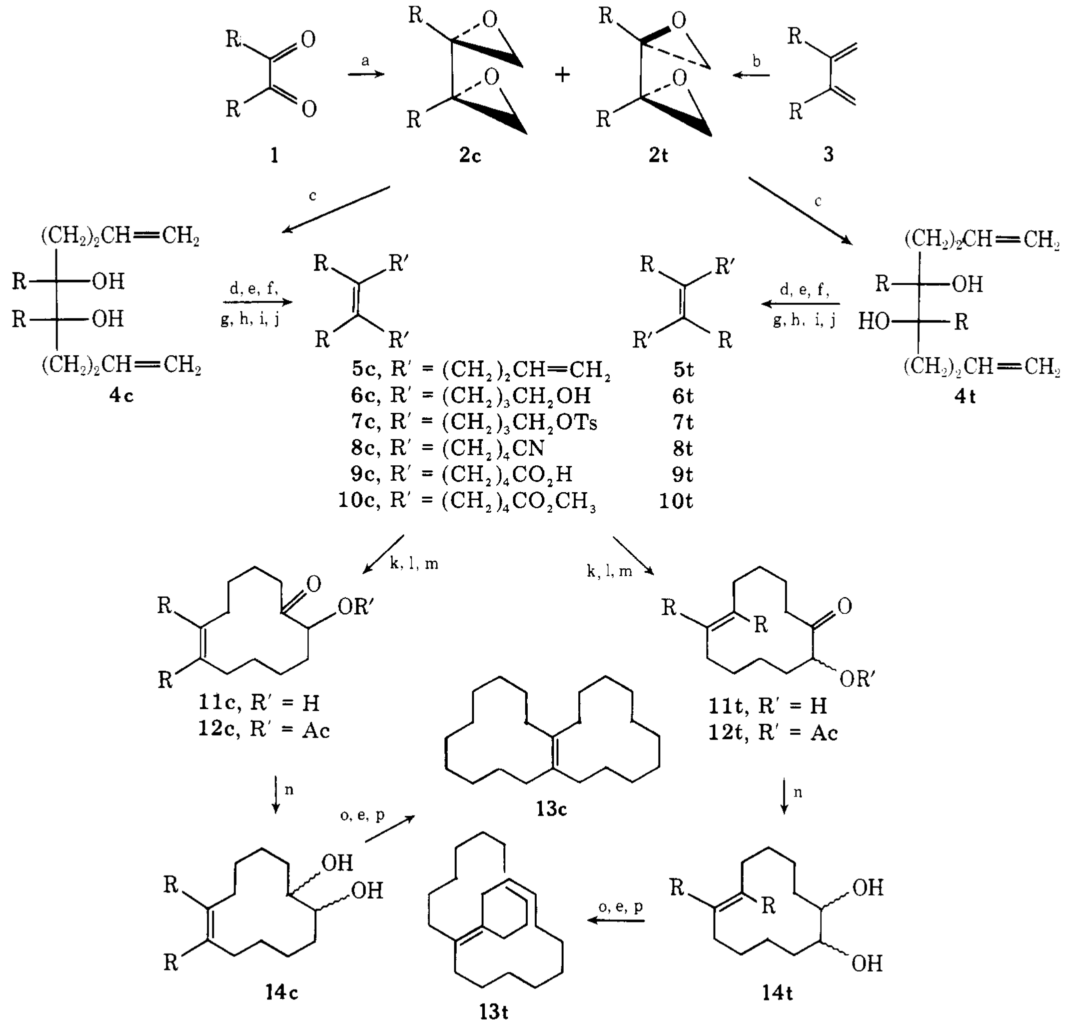
Treatment of cyclododecane-1,2-dione (**1**),[9] with dimethylsulfonium methylide[10] in dimethyl sulfoxide afforded a 1.5:1 mixture of the trans (**2t**) and cis (**2c**) bisepoxides, separable by chromatography on silica gel. Direct expoxidation of 1,2-dimethylenecyclododecane (**3**)[11] with *m*-chloroperoxybenzoic acid yielded the same two epoxides as a 2:1 mixture favoring the cis isomer **2c**. The stereochemistry of these substances was established through their reduction in quantitative yield with lithium aluminum hydride to *cis*- and *trans*-1,2-dimethylcyclododecane-1,2-diol.[12,13]

The trans bisepoxide **2t** smoothly gave diol **4t**, mp 112–113 °C, upon treatment with allyllithium in ether–benzene. Likewise, the cis bisepoxide **2c** was converted to the cis diol **4c**, mp 72–73 °C, in 90% yield. Alternatively, the cis diol **4c** could be secured directly as the exclusive product of addition of 3-butenyllithium to cyclododecane-1,2-dione (**1**). Each of the isomeric diols **4t** and **4c** was converted to the corresponding triene **5t** with roughly 90% stereochemical retention through lithium–ammonia reduction of the cyclic ethyl phosphate derivative.[13] The phosphates were prepared by treatment of each diol with *n*-butyllithium in hexane–tetrahydrofuran followed by ethyl phosphorodichloridate.[14]

We next carried out a standard sequence of reactions to effect side chain homologation of trienes **5t** and **5c** leading ultimately to diesters **10t** and **10c** in greater than 60% overall yield (Chart I). Preliminary studies indicated that the same diesters would be obtained less efficiently through addition of 3-butenyllithium to epoxides **2t** and **2c** followed by subsequent side chain terminal oxidation (disiamylborane[15] and then chromic acid[16]).

After numerous trials with alternative procedures, we found sodium–potassium alloy in refluxing xylene containing tri-

Chart I.[a] [R,R = $(CH_2)_{10}$]



[a] (a) $(CH_3)_2S^+{-}CH_2^-$; (b) *m*-$ClC_6H_4CO_3H$; (c) $CH_2{=}CHCH_2Li$; (d) *n*-BuLi, Cl_2PO_2Et; (e) Li, NH_3; (f) R_2BH, H_2O_2, NaOH; (g) TsCl, C_5H_5N; (h) NaCN; (i) KOH, HCl; (j) CH_2N_2; (k) Na-K, xylene, Me_3SiCl; (l) *n*-Bu_4NF; (m) Ac_2O, C_5H_5N; (n) $LiAlH_4$; (o) *n*-BuLi; Cl_2PONMe_2; (p) H_2/Pt.

methylsilyl chloride to be most satisfactory for effecting the acyloin cyclization of diesters **10t** and **10c**.[17] The resulting enediol trimethylsilyl ethers were cleaved with tetra-*n*-butylammonium fluoride[18] to give hydroxy ketones **11t** and **11c**. These were directly acetylated to the corresponding acetates **12t** and **12c**. Whereas acetate **12c** appeared homogeneous according to spectral properties, chromatographic behavior, and melting point (173–174 °C), the isomeric acetate **12t** exhibited doubled peaks in its NMR spectrum and gave two closely spaced peaks upon high pressure liquid chromatography indicative of a roughly 40:60 mixture. Such behavior is to be expected from the betweenanene isomer which, owing to chirality of the ring system, should be produced as a diastereomeric mixture by the above described reaction sequence. Acetate **12c**, on the other hand, lacking a chiral ring system, should be formed as a *dl* pair.

Reduction of keto acetates **12t** and **12c** with lithium aluminum hydride yielded diols **14t** and **14c** as an apparent mixture of diastereoisomers. Each of these mixtures was converted to the cyclic phosphoramidate by treatment with *n*-butyllithium followed by dimethyl aminophosphorodichloridate.[13] Exposure to lithium in ammonia effected reduction–elimination to the corresponding disubstituted olefins[13] (mixture of cis–trans isomers) which were in turn hydrogenated to [10.10]betweenanene (**13t**), mp 64–65 °C, and bicyclo-[10.10.0]docos-1(12)-ene, mp 136–138 °C.

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(8) The name "betweenanene" is derived from the spatial arrangement of the lower members of the family wherein the double bond ("ene") is sandwiched "between" the alkyl ("ane") chains. The bracketed numerical prefixes indicate the number of carbons in each of the chains analogous to the familiar Baeyer scheme for naming bridged alicyclic compounds. The nomenclature scheme is reserved for the trans bicyclic olefins. The cis isomers can be named using the Baeyer system as indicated for olefin **13c**. While Baeyer's system might be used in conjunction with the *E,Z* convention to name bicyclic olefins with unequal values of *a* and *b* (structure II), it fails to distinguish the isomers having identical bridging chains (*a* = *b*) such as **13c** and **13t**. The betweenanenes may be viewed

as the aliphatic counterparts of layered cyclophanes. Cf. T. Otsulo, S. Mizogami, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 2457 (1973); D. T. Longone and H. S. Chow, *J. Am. Chem. Soc.*, **92,** 994 (1970).
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Asymmetric Synthesis in Liquid Crystals: Independence of Stereochemistry on the Handedness of the Cholesteric Liquid Crystal

Sir:

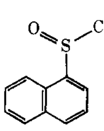
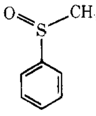
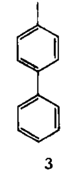
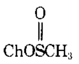
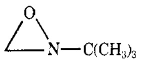
Two groups have recently reported asymmetric transformations induced solely by the use of cholesteric liquid crystals as chiral reaction media.[1,2] Saeva found that the Claisen rearrangement of methylallyl *p*-tolyl ether affords optically active 2-(α-methylallyl)-4-methylphenol when conducted in cholesteryl *p*-nitrobenzoate (ChNB);[1] Verbit found that decarboxylation of ethylphenylmalonic acid in cholesteryl benzoate (ChB) gives (*R*)-(−)-2-phenylbutyric acid of 18% enantiomeric excess.[2] Verbit has suggested[2] that the helical macrostructure of the cholesteric mesophase rather than the "local" asymmetry of the steroid system controls the stereochemical sense of the asymmetric transformation. He further postulated that had the decarboxylation of ethylphenylmalonic acid been conducted in a cholesteric liquid crystal of the opposite macrostructural handedness, the opposite enantiomer of the α-phenylbutyric acid would have been obtained in excess.

We now report the use of cholesteric liquid crystalline reaction media to cause interconvertible enantiomers to assume a nonracemic composition. We also offer evidence that factors other than the macrostructural handedness of the mesophase controls the stereochemical outcome of such equilibrations.

Sulfoxides have appreciable barriers to inversion at sulfur and generally racemize only at temperatures above 150 °C.[3] When low concentrations (<5%) of racemic sulfoxides are dissolved in cholesteryl esters and heated in sealed degassed ampules at temperatures such as to maintain the liquid crystal in the cholesteric mesophase, the enantiomeric composition of the sulfoxides can be changed. After heating, the sulfoxides were recovered (>80%) by chromatographing the entire contents of the ampule upon silica gel. The enantiomeric compositions and absolute configurations of the thus purified sulfoxides were determined by polarimetry or by NMR[4,5] using a chiral solvating agent such as 2,2,2-trifluoro-1-(1-naphthyl)ethanol.[6]

In general, the sulfoxides show small but reproducible amounts of asymmetric induction (0–9% e.e.) comparable in magnitude to those observed for oxidation of sulfides by chiral peracids. Table I shows the results of several such equilibra-

Table I. Equilibration[7] of Enantiomers in Cholesteric Liquid Crystals

Solute	Solvent	*T*, °C	Time, hr	E.e.[a]	Configuration[b]	Solute/solvent[c]	Transition temp[d]	
							Solid–Chol	Chol–Isotropic
 **1**	ChB	145	6	2.4	*R*	100/2.5	145	162
	ChNB	190	3	9.2	*R*	100[e]/2.0	182	230–260 dec
	ChDCB	150	6	0		100/2.5	129	196
	ChN	170	3	1.0	*S*	150/3.0	165	222
	ChC	175	3	1.4	*S*	100[e]/2.5	158	195
	ChS	200	2	1.4	*S*	40/0.9		
	ChPB	175	3	2.4	*S*	100/2.5	156	220
 **2**	ChNB	190	3	2.4	*R*	100[e]/2.5	182	220–260 dec
	ChT	110	4	0		100/2.0	110	123
 **3**	ChNB	190	3	6	*S*	100[e]/2.5	182	254 dec
	ChPB	190	3	<3	*R*	100/2.5	161	226
 $\overset{\overset{\displaystyle O}{\|}}{\mathrm{ChOSCH_3}}$ **4**	ChDCB	100–140[f]	8	6.8	*S*	1000/1.0	108	185
	ChB	145	0.5	16.9	*R*	250/3.0	131	153
	ChL	85	2	12.3	*R*	100/1.5	76	86
	Toluene	110	3	20	*S*			
	ChL (isotropic)	110	3	5	*S*	100/1.5		
 **5**	ChB	148	0.08	20		100/2.0	147	183

[a] Enantiomeric excess. [b] Absolute configuration of major enantiomer. [c] Milligrams of solute/gram of solvent, solute and solvent were sealed in an ampule under vacuum, and the ampule was slowly rotated in an oil bath or oven for the specified time. [d] Determined by differential thermal analysis. [e] It was verified by CD[9] that this mixture has the same pitch handedness under the reaction condition as that of the pure ester. [f] Exhibits the frozen cholesteric mesophase. Mixture was heated to 140 °C, mixed, then cooled and kept at 100 °C.