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Photochemically Induced Skeletal Rearrangement of Alkyl Substituted Indenes[1]

Sir:

Previous studies of the photochemistry of indene and alkyl substituted indenes have dealt with the sensitized dimerization of indene systems.[2] Indene itself is reported to "polymerize" upon direct irradiation, and direct irradiation of 1,1-dimethylindene gives no reported monomeric products.[2] This contrasts with 1,1-diphenylindenes which, upon irradiation, give rearrangement products resulting from phenyl migration to the indene 2 position.[2,3] We now wish to report the photorearrangement of certain alkyl substituted indenes.

A number of alkyl substituted indenes were photolyzed at 25 °C in dilute hydrocarbon (cyclohexane or *n*-hexane) solutions (ca. 10^{-2} M) in evacuated, sealed, quartz photolysis tubes. Photoproducts were isolated (preparative GLC) and identified by a comparison of spectral data (^{1}H NMR, IR) with authentic sample spectra. Quantum efficiencies of product formation (Φ_{pdt}) and loss of starting material (Φ_{dis}) were determined by analytical GLC analysis relative to the trans to cis photoisomerization of 1-phenyl-2-butene.[4] The indenes studied, their photoproducts, and measured quantum efficiencies are presented in Table I.[5]

The observed photorearrangement, as depicted with 2-ethyl-1-methylindene, is an exchange of the indene 1 and 2 carbons, with the formation of an approximately equimolar ratio of the possible indene olefin isomers. This photorearrangement is observed only for indenes substituted at the 1 and 2 positions. (The introduction of an alkyl group at the 3 position essentially quenches the rearrangement.) The presence of at least one alkyl substituent at the 1 or 2 position is required since McCullough reports that no deuterium scrambling is observed upon irradiation of 1,1,3-trideuterioindene.[2]

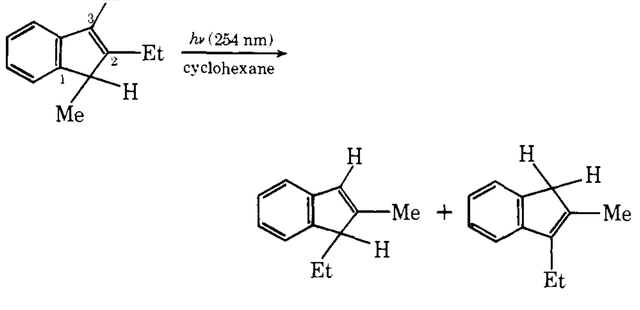
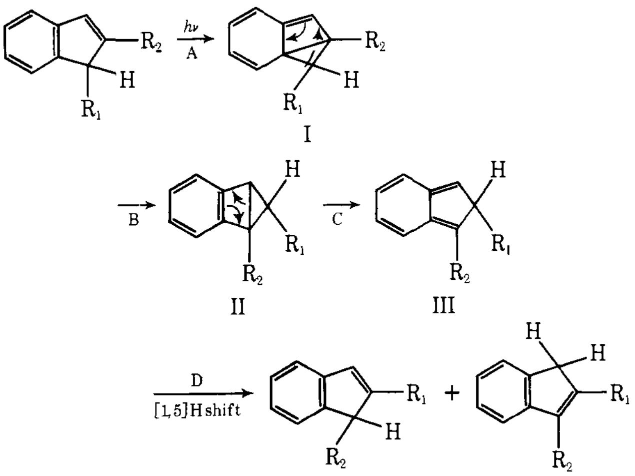


Table I. Substituted Indene Photoproducts and Quantum Efficiencies[a]

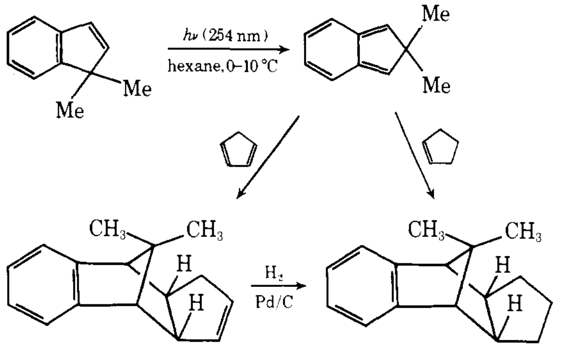
Starting material	Φ_{dis}	Photoproduct(s)	Φ_{pdt}
1-Methylindene	0.16	2-Methylindene	0.03
2-Methylindene	0.13	1-Methylindene	0.03
		3-Methylindene	0.02
3-Methylindene	0.12	None	—
1,3-Dimethylindene	—	None	—
2-Ethyl-1-methylindene	0.23	1-Ethyl-2-methylindene	0.12
		3-Ethyl-1-methylindene	0.10
1,1-Dimethylindene	—	2,2-Dimethylisoindene	—

[a] All photolyses in dilute hydrocarbon solutions, at 25 °C.

Scheme I. Proposed Rearrangement Mechanism



Irradiation of 1,1-dimethylindene gives 2,2-dimethylisoindene (2,2-dimethyl-2*H*-indene) as the sole product. Photolysis of a hexane solution (10^{-2} M) of 1,1-dimethylindene at 0–10 °C can be used to produce solutions of 2,2-dimethylisoindene, in 10–15% concentration relative to 1,1-dimethylindene.[6,7] These solutions are stable for several days at −20 °C and for 1–2 h at 25 °C.[8] UV and emission spectroscopy examinations of room temperature solutions of 2,2-dimethylisoindene show long wavelength absorption in the 330–430-nm region with maxima at 370, 398, and 423 nm, and an emission maximum at 456 nm.[9] (By comparison, *o*-xylylene has an absorption maximum (EPA, 77 K) at 373 nm and an emission maximum at 446 nm).[10] The presence of 2,2-dimethylisoindene was further confirmed by Diels–Alder trapping of the isoindene at 25 °C, with cyclopentadiene and cyclopentene.



A mechanism that explains the above rearrangements is presented in Scheme I. An initial [2 + 2] photocycloaddition

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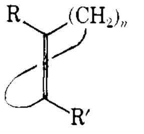
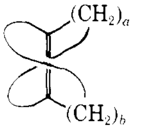
[10.10]Betweenanene: the First Known Member of a Novel Class of Fused Bicyclic Trans Cycloalkenes

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-