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(6) The procedure utilized was identical with that previously described for the preparation of allylic pseudoureas: S. Tsuboi, P. Stromquist, and L. E. Overman *Tetrahedron Lett.*, 1145 (1976).

(7) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1003 (1953).

(8) All new compounds were fully characterized by spectral means (^{1}H and ^{13}C NMR, IR, mass) and elemental composition.

(9) We anticipate that this side-reaction will be suppressed (or eliminated) by the use of gas phase (hot tube) pyrolysis techniques. This aspect is under investigation.

(10) (a) L. E. Overman and L. A. Clizbe, *J. Am. Chem. Soc.*, **98**, 2352 (1976); (b) *ibid.*, **98**, 8295 (1976).

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(12) For example, thermolysis of the trichloroacetimidic ester of 3-butyn-2-ol affords (*Z*)-1-trichloroacetamido-1,3-butadiene as the major isomer (kinetic preference 98:2).[10b] Similarly thermolysis of pseudourea **1** (R_1 = CH_3, R_2 = H, xylene, 137 °C, 2 h) affords, in addition to 5-ethyl-4-methyl-2-pyrrolidinyloxazole, a diene (7% yield, ca. 90% pure) which was clearly (^{1}H and ^{13}C NMR) not the (*E*),(*E*)-isomer **9**, but rather the 1-(*Z*),3-(*E*) isomer.

(13) F. Eloy and A. Deryckere, *J. Heterocycl. Chem.*, **7**, 1191 (1970); *Chim. Ther.*, 416 (1970); J. H. MacMillan and S. S. Washburne, *J. Org. Chem.*, **38**, 2982 (1973).

(14) A. P. Sloan Foundation Fellow, 1975–1977; Camille and Henry Dreyfus Teacher-Scholar Award Recipient, 1976–1981.

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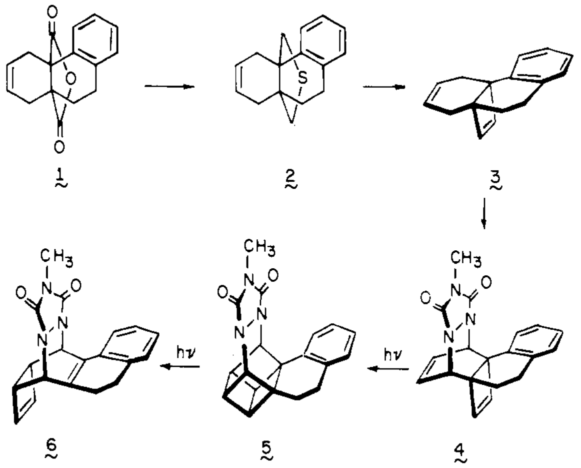
Stereospecific [3,3] Shift of a Cyclobutene Ring Involving Photofragmentation of a 1,8-Bishomocubane as the Relay

Sir:

During recent years, the chemistry of homo- and bishomocubane derivatives, in particular the susceptibility of such compounds to metal-catalyzed rearrangement,[1] has received considerable attention.[2] These highly strained molecules owe their stability in large part to orbital symmetry constraints which preclude simple $[_\sigma 2_s + {}_\sigma 2_s]$ thermal retrogression.[3-5] Although one might hope to avail himself of the synthetic potential of such cycloreversions by the utilization of photochemical methods, these ring systems have also proven stable to light. In fact, intramolecular photocyclization constitutes their most important method of synthesis. We now report a novel photorearrangement mediated by a 1,8-bishomocubane derivative in which a suitably positioned benzene ring serves as the internal activator. The key feature of the process is a stereospecific [3,3]cyclobutene ring transposition which provides a route along an excited state hypersurface from unsaturated propellanes to cyclooctatetraenes.[6]

In a sequence modeled after that devised earlier for cyclobutene annulation,[9] anhydride **1**[10] was converted to the tetracyclic sulfide **2** in 76% overall yield. Successive treatment of **2** with 1 equiv of *N*-chlorosuccinimide and 2 equiv of monoperphthalic acid gave a mixture of α-chlorosulfones which without purification was subjected to suitable Ramberg-Bäcklund rearrangement conditions (KO-*t*-Bu, THF, reflux, 2.5 h). The resulting hydrocarbon (**3**) could be readily purified by column chromatography on alumina (52% from **2**): (δ, $CDCl_3$) 7.31–7.06 (m, 4), 5.84 (m, 3), 5.64 (d, *J* = 3 Hz, 1), 2.84–2.54 (m, 3), 2.29 (m, 1), 2.01 (m, 2), and 1.87–1.16 (m, 2).

Adduct **4** was obtained from **3** by selective bromination of the cyclohexene double bond (Py·HBr_3, HOAc/CCl_4), twofold dehydrobromination (LiCl, Li_2CO_3, HMPA, 90 °C) to introduce the bicyclo[4.2.0]octatriene part structure, and reaction with *N*-methyltriazolinedione in ethyl acetate at −70 °C (56% overall). That entry of the dienophile had occurred from that surface anti to the cyclobutene ring was suggested by Eu(fod)$_3$-induced shifting experiments and substantiated by the photochemical behavior of **4**.



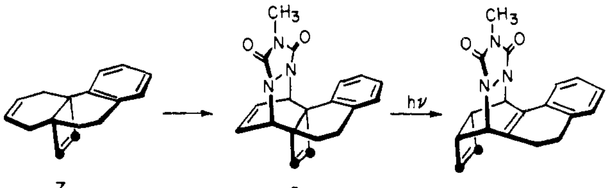
Irradiation of a benzene-acetone (1:1) solution of **4** through Corex with a 450-W Hanovia lamp for 3 h resulted in conversion to **5**, mp 148–150 °C,[11] and **6**, mp 147–147.5 °C[12] (71 and 25% yields based upon unconsumed **4** after silica gel chromatography). At shorter reaction times, the relative percentages of **6** were appreciably less. Since bishomocubane **5** independently undergoes photofragmentation to **6** under these conditions, it is seen to be the intermediate linking **6** to **4**. The structural assignment to **6** has been firmly established by three-dimensional x-ray crystal structure analysis.

Photoproduct **6** crystallized in the monoclinic space group with a = 11.886 (6) Å, b = 8.453 (2) Å, c = 15.878 (2) Å, and β = 92.54 (3)°. The systematic extinctions conformed to $P2_1/n$ and a density measurement indicated Z = 4 or one molecule of $C_{19}H_{17}O_2N_3$ formed the asymmetric unit. All unique diffraction maxima within the 2θ sphere of 110° were measured using graphite monochromated Cu Kα (1.5418 Å) x rays. A total of 2269 diffraction maxima were surveyed and after correction for Lorentz, polarization, and background effects, 1754 were judged observed ($F_o \geq 3\sigma(F_o)$).

The structure was solved routinely using a multisolution weighted tangent formula approach.[13] Full-matrix least-squares refinements with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogens smoothly converged to a standard crystallographic discrepancy index of 0.046 for the observed reflections.[14] The computer generated drawing of the final x-ray model, bond distances, and angles which are presented in the supplemental material agree well with generally accepted values; see paragraph at end of paper regarding supplementary material. The cyclobutene ring is clearly joined in exo fashion to the bicyclic ring. There are no abnormally close intermolecular contacts or large residual peaks in a final difference electron density synthesis.

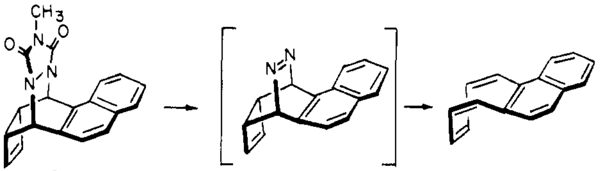
As a test of the regiodisposition of this photorearrangement, dideuteriopropellane **7** was prepared. Its synthesis was accomplished by H/D exchange at the α-chlorosulfone stage

(NaOD, D_2O, dioxane) prior to Ramberg–Bäcklund rearrangement.[15] Subsequent elaboration of **8** resulted in introduction of the diagnostically useful isotopic labels into the cyclobutene sites. Photoisomerization of **8** provided **9** in addition to the anticipated bishomocubane-d_2. The ^1H NMR spectrum of **9** proved identical with that of **6** except that the two-proton olefinic absorption was now lacking and the multiplicities of the cyclobutyl protons were somewhat permuted. Unquestionably therefore, the trigonal cyclobutene carbons have formally maintained their integrity during the [3,3] shift.



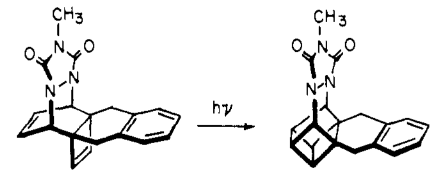
7 **8** **9**

When urazole **6** was irradiated with a tungsten lamp in the presence of *N*-bromosuccinimide (CH_2Cl_2 solution), HBr was lost spontaneously to give **10** directly (90%). Hydrolysis of **10** with boiling NaOH-*i*-PrOH under argon followed by MnO_2 oxidation of the resulting semicarbazide gave cyclooctatetraeno[*a*]naphthalene[16] (**12**, 70%), presumably via unstable azo compound **11**.



10 **11** **12**

A hypothetical scheme for effecting the cleavage of **5** would involve homolytic rupture of that cubyl edge bond which gives rise in part to a benzylic free radical center.[17] Once this has occurred, introduction of the styrene and cyclobutene double bonds can result from cleavage of a second proximal strained bond. Alternatively, the ring opening may follow a concerted $[_\sigma 2_s + {}_\sigma 2_s]$ retrogression pathway. At the present time, no distinction can be made between these options. Notwithstanding, there are good reasons to believe that the ability to develop extended conjugation with the benzene ring at the transition state is a prerequisite for ring opening. For example, comparable irradiation of isomer **13** rapidly leads to **14** (93%), but the latter is entirely stable even for extended reaction periods.[18] Therefore, in the absence of the special effects introduced by a properly positioned fused aryl substituent, the generally recognized photochemical inertness of the 1,8-bishomocubyl framework is restored.[19]



13 **14**

Supplementary Material Available: The crystallographic data for **6** (fractional coordinates (Table I), bond distances (Table II), and bond angles (Table III), together with observed and calculated structure factors (Table IV)) and a computer generated drawing of the final x-ray model (14 pages). Ordering information is available on any current masthead page.

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(12) $\delta_{Me_4Si}{}^{CDCl_3}$ 7.32–7.07 (m, 4), 5.94 (m, 2), 5.42 (m, 1), 4.83 (m, 1), 3.36 (m, 2), 2.92–2.68 (m, 2), 2.92 (s, 3), and 2.52–2.17 (m, 2).

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(17) As analogy, consult G. Kaupp and K. Krieger, *Angew. Chem.*, **84**, 719 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 719 (1972).

(18) These data were first obtained in these laboratories by Dr. Tomas Kempe.

(19) This work was supported in part by a grant (CA-12115) from the National Institutes of Health.

(20) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee, 1972–1977.

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Photoisomerization of 4-Hydroxypyrylium Cations. Furyl Cation Formation

Sir:

Previous reports have shown that 4-hydroxypyrylium cations undergo photoisomerization to 2-hydroxypyrylium cations.[1-4] We now wish to report that 2,3-dimethyl-4-hydroxypyrylium cation **1a** and 2-methyl-3-ethyl-4-hydroxypyrylium cation **1b** undergo photoisomerization to yield furyl cations **2a** and **2b**, respectively, as the major products. In these instances, 2-hydroxypyrylium cations **3a** and **4a** or **3b** and **4b** were observed as additional products.