the UV desorption experiment and confirms that the photodesorption rate measured is not strongly influenced by thermal effects. The inset to Figure 2 shows the mass spectrometer detection of photodesorbing CO during the first 0.17 h of exposure to UV radiation.

The C-H activation experiment was carried out over $Rh(CO)_2/Al_2O_3$ (2.2% Rh) in the presence of 2.40 Torr of spectroscopically pure (>99.5%)[25] cyclohexane, $c\text{-}C_6H_{12}$. Figure 3 shows the C-H IR stretching region, measured after pumping the gas-phase $c\text{-}C_6H_{12}$ away. A strongly bound hydrocarbon species is observed to increase in coverage for increasing irradiation time. CO photodesorption is slow compared to that in vacuum because of CO(g) diffusion limitations in the presence of the high pressure of $c\text{-}C_6H_{12}$ (or He). The C-H stretching mode frequencies for the bound alkyl species are very similar to those of $c\text{-}C_6H_{12}$ and are attributed to the cyclohexyl species. The chemisorbed cyclohexyl species we observe is thermally rather stable on the surface, as shown in the inset to Figure 3, where it is observed in vacuum up to 600 K. This stability may indicate that cyclohexyl species transfer to the Al_2O_3 support after formation on the Rh center. Thermal and photochemical control experiments with only $c\text{-}C_6H_{12}$ over Rh/Al_2O_3 (no adsorbed CO) produced only trace amounts of cyclohexyl(a) species. It is postulated that the initial C-H activation process observed here is

$$Rh(CO)_2(a) \xrightarrow{h\nu} [Rh(CO)(a) + CO(g)] \xrightarrow{c\text{-}C_6H_{12}} Rh(CO)(H)(C_6H_{11})(a)$$

Efforts are underway to characterize the postulated product by detailed IR measurements.[26] This is the first report of C-H bond activation in alkanes by this type of photochemistry on a solid surface.

(25) Gas chromatography analysis indicates <10 ppm of cyclohexene or benzene impurity.

(26) Ballinger, T. H.; Yates, J. T., Jr. *J. Phys. Chem.*, in press. Wong, J. C. S.; Ballinger, T. H.; Yates, J. T., Jr. Manuscript in preparation.

Synthesis and Rearrangement Reactions of the First *trans*-Homotropone

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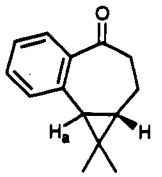
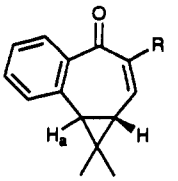
We recently described an efficient synthesis of the strained *trans*-benzobicyclo[5.1.0]octene **1** via photoisomerization of the cis isomer **2**.[1] Herein we report that a significant extension of this approach has now furnished **3**, the first *trans*-homotropone. Considerable research in the homotropone area has confirmed the homoaromatic stabilization of suitable cis-fused [5.1.0] bicyclic systems.[2] In the heretofore elusive trans species, the orbitals best aligned for homoconjugation reside on the central cyclopropane bond; accordingly, these structures are expected to manifest Möbius antihomoaromatic destabilization.[3] As anticipated, both **3** and the isomeric *cis*-benzohomotropone **4** undergo facile thermal and photochemical rearrangements.

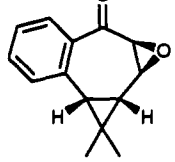


1 α-H_a
2 β-H_a



3 α-H_a, R = H
4 β-H_a, R = H
15 β-H_a, R = D

Initially we sought to prepare **3** via direct photoisomerization of **4**,[4] the latter readily obtained via Saegusa oxidation of the silyl enol ether derived from **1** (87% yield, two steps).[5,6] However, irradiation of **4** induced marked skeletal rearrangement (vide infra), so we turned to a β-elimination tactic. Epoxidation of **4** (TBHP, Triton B, 93%)[7] followed by SmI_2-mediated ring opening[8] of the resultant oxirane **5**[4] (THF, −90 °C, 35%) afforded β-hydroxy ketone **6**.[4] Photolysis of **6** in hexanes (0.05 M, 2 h, Pyrex) produced a 2:1 mixture of diastereomeric *trans*-cyclopropanes **7**[4] and **8**[4] in 59% yield,[9] accompanied by recovered **6** (37%). Acetylation (Ac_2O, DMAP, CH_2Cl_2, 89%) gave **9**[4] and **10**,[4] respectively, and single-crystal X-ray analysis secured the formulation of **10**. Both acetates in turn furnished **3** upon exposure to DBU in benzene (room temperature, 30 min). Silica flash chromatography of the crude mixture unexpectedly generated naphthol **11** in 50% yield;[10] the striking lability of **3** contrasts with the unremarkable behavior of **4**, which can be purified in standard fashion. We then devised a viable chromatographic protocol[11] which provided pure **3**[4] as an oil (ca. 80% yield); the product was characterized spectroscopically and by L-Selectride-mediated 1,4-reduction[12] to **1**, a trans-fused structure previously established by crystallography.[1]



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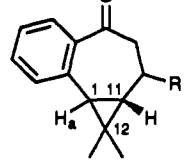
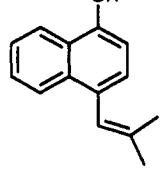


6 β-H_a, R = β-OH
7 α-H_a, R = β-OH
8 α-H_a, R = α-OH
9 α-H_a, R = β-OAc
10 α-H_a, R = α-OAc



11

We have also explored the thermal and photochemical reactivity of the *trans*- and *cis*-benzohomotropones **3** and **4**. Upon heating in *o*-dichlorobenzene-d_4 at 70 °C, **3** underwent a vinylcyclopropane rearrangement to furnish **12**[4] almost quantitatively. Kinetic data obtained via ^1H NMR established that the reaction is first-order, with an Arrhenius activation energy of 26.1 kcal/mol and an entropy of activation of −3.6 eu. Under similar conditions, **4**

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(4) The structure assigned to each new compound is in accord with its infrared and high-field ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra, as well as appropriate parent ion identification by high-resolution mass spectrometry.

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(9) The products arose via competing cleavage of the peripheral (C1,12) and central (C1,11) benzylic cyclopropane bonds in **6**. Factors influencing the partitioning between central and peripheral bond scission will be discussed in the full account of our photoisomerization studies.

(10) For a likely isomerization mechanism, see: Childs, R. F.; Varadarajan, A. *Can. J. Chem.* **1981**, *59*, 3252.

(11) Chromatography on neutral "alumina adsorption" (Fisher Scientific, 80–200 mesh, used as received) with Et_3N-doped eluant suppressed the facile formation of **11**.

(12) Fortunato, J. M.; Ganem, B. *J. Org. Chem.* **1976**, *41*, 2194.

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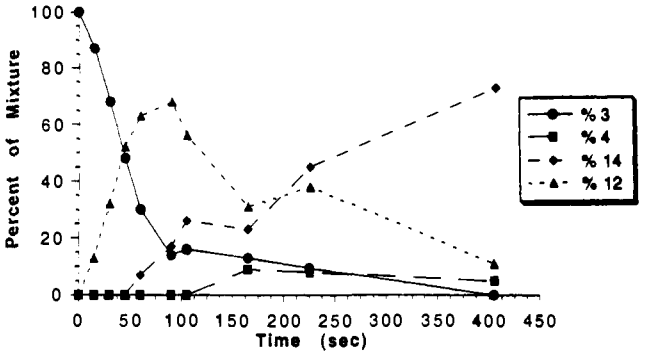
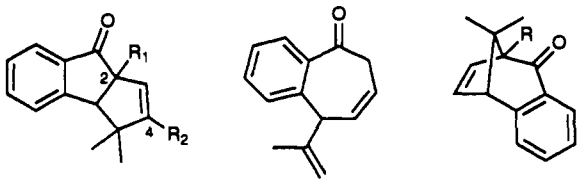


Figure 1. ^{1}H NMR monitoring of the photolysis of *trans*-homotropone **3**.

isomerized via a well-precedented [1,5] sigmatropic shift,[13a] resulting in quantitative conversion to **13**.[4] The latter process also proved to be first-order, with E_a = 29.9 kcal/mol[13b] and $\Delta S^{\ddagger}$ = −3.3 eu. The exceptionally low activation energy[14] for rearrangement of **3** reflects the additional strain imparted by the trans ring fusion.[15]



12 $R_1 = R_2 = H$
16 $R_1 = H, R_2 = D$
18 $R_1 = D, R_2 = H$

13

14 R = H
17 R = D

Irradiation of **4** in benzene (0.4 M, 0.5 h, Pyrex)[16] led to ketone **14**[4] as the only isolable product (28% yield, 57% based on recovered **4**). In contrast, the photolysis of **3**, monitored by ^{1}H NMR at 15-s intervals as illustrated in Figure 1, cleanly generated a mixture of **4**, **14**, and **12**. The data revealed fast initial formation of *cis*-homotropone **4** and suggested that **14** then derived from **4**, and **12** in turn from **14**. Support for this scheme followed from deuterium-labeling studies, wherein irradiation of **15** (82% D) afforded **16** labeled only in the C(4) vinyl position (81% D). The product presumably derived from Norrish type I cleavage of **17** and radical recombination; an excited-state vinylcyclopropane-type rearrangement[17] of **15** would have furnished **18**, containing the deuterium label at C(2).[18]

In summary, we have prepared the first *trans*-homotropone and characterized its thermal and photochemical reactivity. An experimental evaluation of Möbius antihomoaromaticity in **3** and the corresponding oxonium ions will be described in due course.

Acknowledgment. Support for this work was provided by the National Institutes of Health (National Cancer Institute) through Grant CA22807. We thank Drs. G. Furst and P. Carroll and Mr. J. Dykins, Directors of the University of Pennsylvania Spectroscopic Facilities, for assistance in obtaining high-field NMR spectra, X-ray crystallographic analyses, and high-resolution mass spectra.

Supplementary Material Available: Complete spectral data for **3**–**14** and tables of experimental details, positional parameters, and thermal parameters for **10** (11 pages). Ordering information is given on any current masthead page.

(13) (a) Ohloff, G. *Tetrahedron Lett.* **1965**, 3795. (b) This value is comparable to activation energies previously reported for similar [1,5] sigmatropic shifts.[14a]

(14) Activation energies of other vinylcyclopropane rearrangements vary from 26.3 to 54.6 kcal/mol. Reviews: (a) Mil'vitskaya, E. M.; Tarakanova, A. V.; Plate, A. F. *Russ. Chem. Rev.* **1976**, *45*, 469. (b) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247.

(15) Wiberg has calculated a 12.1 kcal/mol difference in strain energies for the parent *cis*- and *trans*-bicyclo[5.1.0]octanes: Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

(16) Pyrex test tubes (20 mL) or NMR tubes (Wilmad no. 507) were charged with reactant solutions and irradiated with a 450-W Hanovia mercury vapor lamp (part no. 679A0360) suspended in a water-cooled Pyrex immersion well.

(17) Paquette has described an isomerization, analogous to the conversion of **15** to **16**, which proceeds via central cyclopropane bond cleavage; cf., Paquette, L. A.; Meehan, G. V.; Henzel, R. P.; Eizember, R. F. *J. Org. Chem.* **1973**, *38*, 3250 and references cited therein.

(18) The estimated detection threshold for **18** is ≤5%.

Blue to Type 2 Binding. Copper(II) and Cobalt(II) Derivatives of a Cys112Asp Mutant of *Pseudomonas aeruginosa* Azurin

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Received June 29, 1992

Of the five invariant residues that surround the copper in azurins,[1] the ligand cysteine at position 112 (Cys112) is believed to be especially important in the bonding interactions responsible for the unusual blue copper absorption and electron paramagnetic resonance (EPR) spectra.[2] It is striking that mutagenesis studies of Met121,[3] His46,[3c] and His117[4] have shown that these ligands are not required for a blue copper center, thereby reinforcing the feeling that Cys112 is absolutely essential.[5] To address this issue directly, we have replaced Cys112 with Asp by site-directed mutagenesis.

Cys112 of *Pseudomonas aeruginosa* azurin was substituted with an aspartate using a synthetic azurin gene.[3c] The mutant (Cys112Asp) azurin was expressed in *Escherichia coli* using a T7 RNA polymerase expression system[6] in which azurin is secreted into the periplasm. Cu^{II}- and Co^{II}-Cys112Asp azurins were made by adding the appropriate metal ion to 1 mM to the periplasmic fraction containing crude apoazurin. In contrast to previously published protocols,[3c,7] protein purifications were performed at room temperature under basic conditions by FPLC. Concentrated crude protein solution was passed through Q-Sepharose fast flow resin with 50 mM Tris-Cl buffer (pH 7.8) containing 50 mM

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