

Supplementary Material Available: Reaction scheme for the preparation of **1** and of the phosphoramidite derivative **6** used to incorporate d_5^I in **X**, experimental conditions, and spectral data for compounds **1** and **2** (6 pages). Ordering information is given on any current masthead page.

Alkane Activation and Oxidative Addition to Rh by Photodesorption of Surface Carbonyl Ligands¹

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The activation of the strong C-H bonds in alkanes (RH) by interaction with partially "naked" metal centers in complexes such as $CpRh(CO)_2$ readily occurs in the homogeneous phase, producing $CpRh(CO)(H)R$.³⁻⁹ The active center is generated by photolysis of $CpRh(CO)_2$,¹⁰⁻¹³ and the presence of the transient $CpRh(CO)$ has just been demonstrated.¹⁴ Such a reaction scheme can provide novel pathways for producing various organic compounds from inactive alkanes. A heterogeneous version of this process would be very desirable as a route to alkane activation.

This communication describes the use of a heterogeneous system, Rh/Al_2O_3 , to achieve the same alkane activation chemistry. It is well-known that the chemisorption of CO on supported Rh produces isolated $Rh(CO)_2$ species.¹⁵⁻²³ This produces a characteristic carbonyl doublet in the infrared spectrum, as observed by transmission IR. Figure 1 shows IR spectral changes due to photodecomposition of the $Rh(CO)_2$ species by irradiation at 325 nm. The Rh surface is supported on an electrically heated grid in ultrahigh vacuum.²⁴ By variation of the electrical power

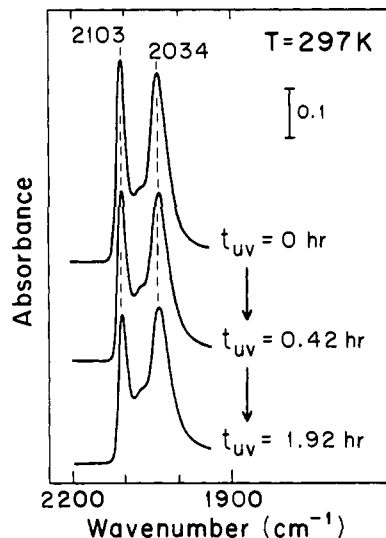


Figure 1. Photodecomposition of $Rh(CO)_2/Al_2O_3$ in vacuum.

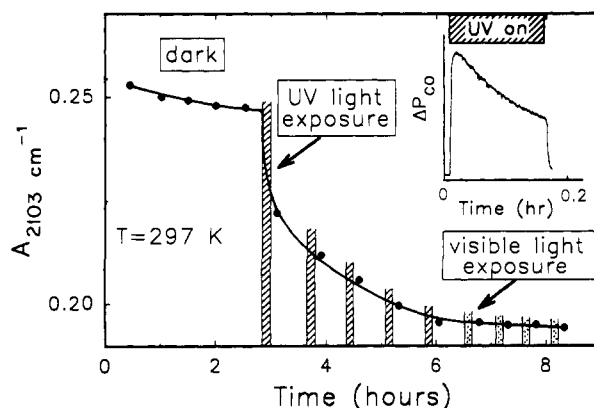


Figure 2. Kinetics of $Rh(CO)_2$ photodecomposition in vacuum by UV light (325 ± 50 nm) compared to visible light at equal power absorption as measured calorimetrically using the grid and thermocouple.

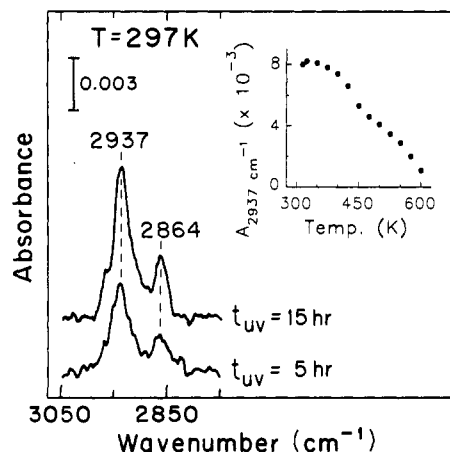


Figure 3. Photochemical production of chemisorbed cyclohexyl species from cyclohexane. Inset shows its thermal stability in vacuum.

(1) Work was supported by the Department of Energy, Office of Basic Energy Sciences.

(2) Cp = η^5 -cyclopentadiene ($\eta^5-C_5H_5$).

(3) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(4) Hoyano, J. K.; Graham, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

(5) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(6) Muetterties, E. L. *Chem. Soc. Rev.* **1983**, *12*, 283.

(7) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Boston, 1984.

(8) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(9) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41.

(10) Belt, S. T.; Grevels, F. W.; Klotzbücher, W. E.; McCamley, A.; Perutz, R. N. *J. Am. Chem. Soc.* **1989**, *111*, 8373.

(11) Fischer, E. O.; Bittler, K. *Z. Naturforsch. B* **1961**, *16*, 225.

(12) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Chem. Commun.* **1984**, *1984*, 624.

(13) Rest, A. J.; Whitwell, I.; Graham, W. A. G.; Hoyano, J. K.; McMaster, A. D. *J. Chem. Soc., Dalton Trans.* **1987**, *1987*, 1181.

(14) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315.

(15) Yang, A. C.; Garland, C. W. *J. Phys. Chem.* **1957**, *61*, 1504.

(16) Yates, J. T., Jr.; Duncan, T. M.; Worley, S. D.; Vaughan, R. W. *J. Chem. Phys.* **1979**, *70*, 1219.

(17) Yates, J. T., Jr.; Duncan, T. M.; Vaughan, R. W. *J. Chem. Phys.* **1979**, *71*, 3908.

(18) Solymosi, F.; Sárkány, J. *Appl. Surf. Sci.* **1979**, *3*, 68.

(19) Solymosi, F.; Erdöhelyi, A.; Kocsis, M. *J. Catal.* **1980**, *65*, 428.

(20) Yates, J. T., Jr.; Kolasinski, K. *J. Chem. Phys.* **1983**, *79*, 1026.

(21) van't Blik, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* **1985**, *107*, 3139.

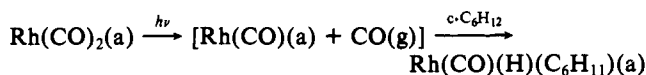
(22) Robbins, J. L. *J. Phys. Chem.* **1986**, *90*, 3381.

(23) Basu, P.; Panayotov, D.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2074.

(24) Basu, P.; Ballinger, T. H.; Yates, J. T., Jr. *Rev. Sci. Instrum.* **1988**, *59*, 1321.

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/Al₂O₃ (2.2% Rh) in the presence of 2.40 Torr of spectroscopically pure (>99.5%)²⁵ cyclohexane, c-C₆H₁₂. Figure 3 shows the C-H IR stretching region, measured after pumping the gas-phase c-C₆H₁₂ 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-C₆H₁₂ (or He). The C-H stretching mode frequencies for the bound alkyl species are very similar to those of c-C₆H₁₂ 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 Al₂O₃ support after formation on the Rh center. Thermal and photochemical control experiments with only c-C₆H₁₂ over Rh/Al₂O₃ (no adsorbed CO) produced only trace amounts of cyclohexyl(a) species. It is postulated that the initial C-H activation process observed here is



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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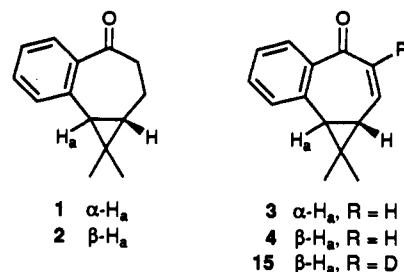
We recently described an efficient synthesis of the strained *trans*-benzobicyclo[5.1.0]octene **1** via photoisomerization of the *cis* isomer **2**.¹ Herein we report that a significant extension of this approach has now furnished **3**, the first *trans*-homotropone. Considerable research in the homotropone 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

(1) Wood, J. L.; Liverton, N. J.; Visnick, M.; Smith, A. B., III. *J. Am. Chem. Soc.* 1989, 111, 4530.

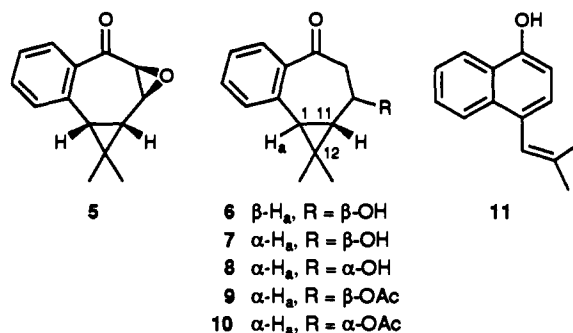
(2) For leading references, see: Childs, R. F. *Acc. Chem. Res.* 1984, 17, 347.

(3) The *trans* ring fusion generates an odd number of nodes in the basis set of orbitals. See: (a) Chapman, O. L.; Fugiel, R. A. *J. Am. Chem. Soc.* 1969, 91, 215. (b) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* 1978, 17, 106 and references cited therein. (c) Staley, S. W.; Kingsley, W. G. *J. Am. Chem. Soc.* 1973, 95, 5804. For examples of charged antihomoaromatic systems, see: (d) Berson, J. A.; Jenkins, J. A. *J. Am. Chem. Soc.* 1972, 94, 8907. (e) Feldman, M.; Flythe, W. C. *J. Am. Chem. Soc.* 1971, 93, 1547. (f) Vogel, P.; Saunders, M.; Hasty, N. M., Jr.; Berson, J. A. *J. Am. Chem. Soc.* 1971, 93, 1551. (g) Childs, R. F.; Varadarajan, A.; Lock, C. J. L.; Faggioli, R.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* 1982, 104, 2452.

3 and the isomeric *cis*-benzohomotropone **4** undergo facile thermal and photochemical rearrangements.



Initially we sought to prepare **3** via direct photoisomerization of **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 SmI₂-mediated ring opening⁸ 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 (Ac₂O, DMAP, CH₂Cl₂, 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 protocol¹¹ which provided pure **3**⁴ as an oil (ca. 80% yield); the product was characterized spectroscopically and by L-Selectride-mediated 1,4-reduction¹² to **1**, a *trans*-fused structure previously established by crystallography.¹



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**

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

(5) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* 1984, 25, 495.

(6) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* 1978, 43, 1011.

(7) Grieco, P. A.; Nishizawa, M.; Oguri, T.; Burke, S. D.; Marinovic, N. *J. Am. Chem. Soc.* 1977, 99, 5773.

(8) Molander, G. A.; Hahn, G. *J. Org. Chem.* 1986, 51, 2596.

(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 Et₃N-doped eluant suppressed the facile formation of **11**.

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