methylsilyl)naphthalene: 27% yield; mass spectrum, *m/e* (percent of base peak) 280 (M^+, 60), 265 (100), 223 (72), 193 (68), 179 (20), 165 (25), 73 (30), 22 (59); HRMS calcd for $[M^+]$ $^{12}C_{19}{}^{1}H_{24}{}^{28}Si$ 280.1647, found 280.1679, calcd for $[M^+ - CH_3]$ $^{12}C_{18}{}^{1}H_{21}{}^{28}Si$ 265.1413, found 265.1414.

1-((Trimethylsilyl)ethynyl)-8-(trimethylsilyl)naphthalene was prepared similarly by using TMSC≡CZnCl[64] in the Pd cross-coupling reaction: 10% yield; mass spectrum, *m/e* (percent of base peak) 296 (M^+, 17), 281 (100), 265 (29), 209 (15), 207 (16), 193 (29), 165 (14), 73 (66); HRMS calcd for $[M^+]$ $^{12}C_{18}{}^{1}H_{24}{}^{28}Si_2$ 296.1417, found 296.1442, calcd for $[M^+ - CH_3]$ $^{12}C_{17}{}^{1}H_{21}{}^{28}Si_2$ 281.1182, found 281.1205.

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Registry No. 1, 536-74-3; 2, 1122-79-8; 3, 124153-61-3; 4, 62618-20-6; 5, 15727-65-8; 8, 124153-63-5; 9, 4250-82-2; 11a, 124153-64-6; 11b, 124153-65-7; 11c, 124153-62-4; 12, 124153-66-8; 13a, 124153-73-7; 13b, 124153-74-8; 13c, 124153-75-9; 13d, 124153-76-0; 13e, 124153-77-1; 13f, 124153-78-2; 14 (R = Me), 1719-19-3; 14 (R = t-Bu), 85051-67-8; 17 (R = t-Bu, *o* isomer), 124153-67-9; 17 (R = t-Bu, *m* isomer), 124153-68-0; 17 (R = t-Bu, *p* isomer), 124153-69-1; 17 (R = Me, *o* isomer), 124153-79-3; 17 (R = Me, *m* isomer), 124153-80-6; 17 (R = Me, *p* isomer), 124153-81-7; 18, 5701-81-5; 21 (*o* isomer), 124153-70-4; 21 (*m* isomer), 124153-71-5; 21 (*p* isomer), 124153-72-6; 25, 74-86-2; 26, 1111-64-4; 27, 1070-75-3; 31, 4440-01-1; tBuC≡CZnCl, 89556-09-2; MeCOMe, 67-64-1; $H_3CCOC(CH_3)_3$, 75-97-8; *m*-BrC_6H_4Br, 108-36-1; *p*-BrC_6H_4Br, 106-37-6; *o*-BrC_6H_4Br, 583-53-9; *m*-$TMSC_6H_4Br$, 17878-47-6; *p*-$TMSC_6H_4Br$, 6999-03-7; *o*-$TMSC_6H_4Br$, 17878-37-4; tBuC≡CH, 917-92-0; TMSC≡CZnCl, 78389-87-4; LiH, 7580-67-8; 1-bromonaphthalene, 90-11-9; 1,8-dilithionaphthalene, 61767-59-7; 1,8-dibromonaphthalene, 17135-74-9; 1-bromo-8-(trimethylsilyl)naphthalene, 124153-82-8; 1-(*tert*-butylethynyl)-8-(trimethylsilyl)naphthalene, 124153-83-9; 1-[(trimethylsilyl)ethynyl]-8-(trimethylsilyl)naphthalene, 124153-84-0.

(69) 73% unreacted 1-bromo-8-(trimethylsilyl)naphthalene: bp ca. 115 °C (0.1 mmHg); mass spectrum, *m/e* (percent of base peak) 280 + 278 (M^+, 5.8), 265 + 263 ($M^+ - CH_3^\bullet$; 49), 183 ($M^+ - [CH_3 + Br^\bullet]$, 100), 167 (15), 155 (14), 141 (23), 115 (19).

The Mechanism of the Olefin-to-Carbene Rearrangement for 9-Phenyl-1(9)-homocubene

Philip E. Eaton* and Andrew J. White

Department of Chemistry, 5735 S. Ellis Avenue, The University of Chicago, Chicago, Illinois 60637

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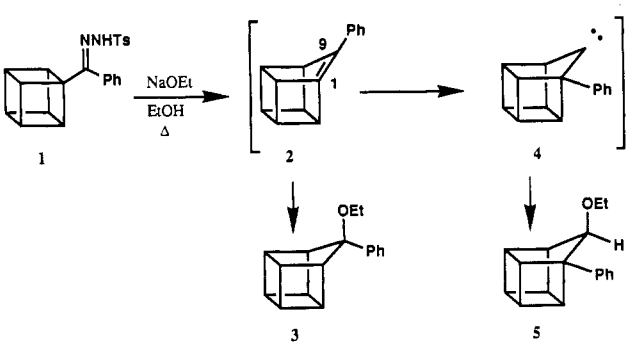
Two distinct mechanistic pathways exist for the olefin-to-carbene rearrangement of 9-phenyl-1(9)-homocubene to 1-phenyl-9-homocubylidene: a phenyl shift or a skeletal carbon–carbon bond shift. Cubane ^{13}C carboxylic acid was prepared and converted to cubyl phenyl ^{13}C ketone and its tosylhydrazone. Determination of the distribution of label in the ethers formed on decomposition of the tosylhydrazone in hot ethanolic base showed that the latter mechanism is operating.

Rearrangements of carbenes to olefins are well-documented in the literature.[1] However, as can be expected from simple energy considerations, only a few examples of the reverse reaction have been observed.[2] These olefin-to-carbene rearrangements apparently can occur only under drastic reaction conditions or when very strained, highly energetic olefins are involved. Little is known about the mechanism of such rearrangements.

Recently, Eaton and Hoffmann[2f] showed that decomposition of cubyl phenyl ketone tosylhydrazone (1) in ethanolic base generated 2, 9-phenyl-1(9)-homocubene, an extraordinarily strained bridgehead olefin. Regiospecific addition of ethanol across the twisted double bond of this very reactive intermediate was proposed to account for

Scheme I



formation of ether 3, one of the reaction products isolated. Rearrangement of olefin 2 to the singlet carbene 4, 1-phenyl-9-homocubylidene, and insertion of this carbene into the O–H bond of ethanol was invoked to account for formation of ether 5, the other isolated product (Scheme I). The ethers are formed in good yield in a ratio of approximately 1.7:1.

The rearrangement of an olefin *to a carbene* is an extraordinary event. How do the bonds reorganize? The p

(1) Gutsche, C. D.; Redmore, D. *Carbocyclic Ring Expansion Reactions*; Academic Press: New York, 1968; pp 111–117.

(2) (a) Billups, W. E.; Lin, L. P.; Chow, W. Y. *J. Am. Chem. Soc.* **1974**, *96*, 4026. (b) Landleer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* **1974**, 2813. (c) Hixson, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 1981. (d) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936. (e) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661. (f) Eaton, P. E.; Hoffmann, K. L. *J. Am. Chem. Soc.* **1987**, *109*, 5285. (g) Chen, N.; Jones, M., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 305.

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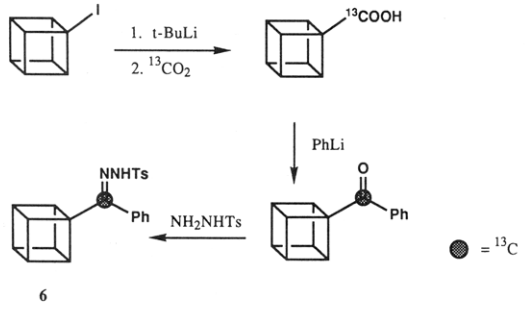
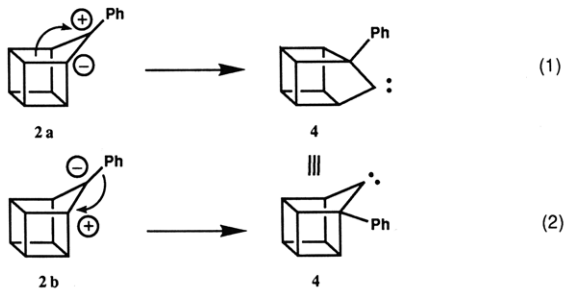
Scheme II



orbitals of the unsaturated carbons in homocubene **2** are twisted well away from the parallel alignment in an ordinary double bond. Indeed, were there no rehybridization of the relevant carbons away from sp^2 the orbitals would be very nearly orthogonal. Some pyramidalization can, however, be expected; the dipolar contributors **2a** and **2b** to the description of the alkene can therefore be considered.[3] The necessary bond reorganization from **2b** for the olefin-to-carbene rearrangement would involve a 1,2-phenyl shift; the original phenylhomocubyl C–C bond would be broken (eq 2). The required reorganization from zwitterion **2a** would involve a skeletal bond migration, but the original phenylhomocubyl C–C bond would remain intact (eq 1). We report now a labeling study done to distinguish these pathways.

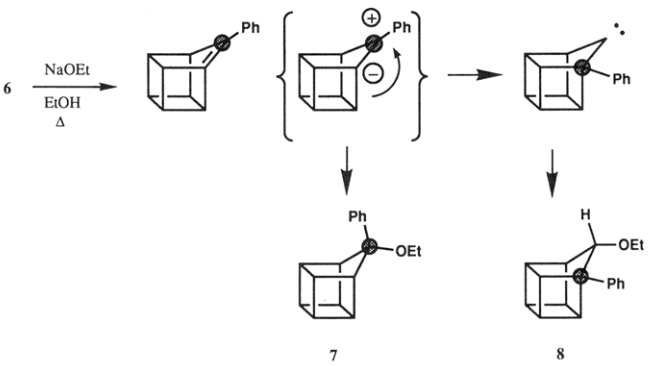


^{13}C-labeled cubyl phenyl ketone tosylhydrazone was readily synthesized from iodocubane in three steps in good yield (Scheme II). Halogen–metal exchange between iodocubane and *tert*-butyllithium in cold THF gave cubyllithium, which was carboxylated with ^{13}C-labeled carbon dioxide. Workup afforded cubane ^{13}C carboxylic acid. Reaction with 2 equiv of phenyllithium gave labeled cubyl phenyl ketone, which was converted to the ^{13}C-labeled cubyl phenyl ketone tosylhydrazone **6** by treatment with tosylhydrazide in ethanol.

Base-induced thermal decomposition of this ^{13}C-labeled cubyl phenyl ketone tosylhydrazone under conditions identical to those employed by Eaton and Hoffmann afforded the two homocubyl ethers **7** and **8** in a ratio of approximately 1.7:1, ^{13}C-labeled, but otherwise corresponding to **3** and **5**.[1] The mixture was analyzed by ^{13}C NMR, comparing its spectrum to those of the separate unlabeled ethers. It was immediately clear that C-9 of ether **7** (δ 101.7 ppm) and C-1 of ether **8** (δ 61.0 ppm) were substantially enhanced; no other enhancements were noticeable (Scheme III).

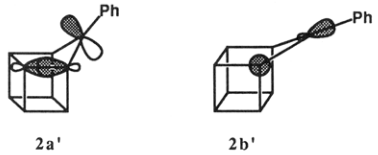
In both ethers the labeled carbon is attached to the phenyl group as it is in the starting material. In ether **7** the label is positioned as required for addition of ethanol to the expected labeled 9-phenyl-1(9)-homocubene before rearrangement.[4] In ether **8**, the location of the label proves

Scheme III



that a skeletal bond migration occurred during the olefin-to-carbene rearrangement rather than a 1,2-phenyl shift. If the phenyl shift mechanism had operated, ether **8** would have had the label not at C-1 but instead at the easily identifiable C-9 ether carbon (δ 96.5 ppm).

This result was predicted a priori by comparison of the two zwitterionic contributors.[2f] The planar benzylic cation in **2a** is expected to be of lower energy than the geometrically constrained, bridgehead nonplanar cation in **2b**. Augmenting this difference, the bridgehead anion in **2a** is favored over the anion in **2b** as it is in an orbital richer in s character. These thermodynamic factors are complemented by (and for the rearrangement are probably secondary to) orbital geometry (kinetic) considerations. The orbitals that would be involved in a 1,2-phenyl shift approach orthogonality (**2b′**) and thus are improperly disposed. On the other hand, those required for the internal skeletal bond shift are reasonably positioned (**2a′**) to accommodate this reorganization.



Experimental Section

Melting points are uncorrected. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. All NMR spectra were run in chloroform-*d* on a Varian VXR-400 spectrometer. ^1H NMR spectra (400 MHz) are referenced to internal tetramethylsilane (0.00 ppm); ^{13}C NMR spectra (100 MHz), to the central line of the chloroform-*d* triplet (77.0 ppm).

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane[^{13}C]carboxylic Acid. Iodocubane[6] (1.7 g, 7.4 mmol) was dissolved in dry THF (30 mL) under nitrogen. The solution was cooled in a −78 °C bath and treated with 15 mL of *t*-BuLi in pentane (Aldrich, 1.35 M, 20.2 mmol) to prepare cubyllithium. The mixture was stirred for 30 min. Separately, $^{13}CO_2$ gas was generated[5] by slow addition of excess concentrated H_2SO_4 onto $Ba^{13}CO_3$ (Aldrich, 3.5 g, 17.5 mmol, 50% label) and bubbled into dry THF (80 mL) at −78 °C. The cubyllithium solution was transferred slowly via cannula to this cold carbonated THF solution. (Overly rapid addition results in the formation of dicubyl ketone.) The reaction mixture was stirred at −78 °C for 0.5 h, warmed to room temperature, and

(3) (a) Salem, L. *Science* **1976**, *193*, 822. (b) Brooks, B. R.; Schaeffer, H. F. *J. Am. Chem. Soc.* **1979**, *101*, 307.

(4) There exists the possibility that, via rearrangement to the carbene and then rearrangement of the carbene to an olefin different from **2**, the label could be scrambled. In this case, there is no evidence for such scrambling. However, as shall be shown in a subsequent paper from this Laboratory (Eaton, P. E.; Appell, R. B. *J. Am. Chem. Soc.*, submitted) that such rearrangements do occur in other cases.

(5) Della, E. W.; Gangodawila, H.; Pigou, P. E. *J. Org. Chem.* **1988**, *53*, 592.

(6) (a) Abeywickrema, R. S.; Della, E. W. *J. Org. Chem.* **1980**, *45*, 4226. (b) The Barton procedure is rather better; cf.: Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

quenched with a saturated aqueous solution of $(NH_4)_2SO_4$. The THF was removed in vacuo on a rotary evaporator with bath temperature maintained below 30 °C. The aqueous phase was washed with diethyl ether (2 × 50 mL), acidified to pH 1 (no lower!) with concentrated hydrochloric acid, salted with NaCl, and extracted with diethyl ether (3 × 50 mL). The extract was dried over $MgSO_4$, filtered, and evaporated leaving a tan solid residue. Crystallization from hexane provided 723 mg (65%) of cubane[^{13}C]carboxylic acid as white crystals: mp 124–125 °C; ^{1}H NMR δ 4.27 (m, 3 H), 4.00 (m, 3 H), 3.98 (m, 1 H) ppm; ^{13}C NMR δ 178.5 (enhanced), 49.4, 47.8, 45.2 ppm.

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octyl Phenyl [^{13}C]Ketone. Phenyllithium in cyclohexane (Aldrich, 9.5 mL, 2 M, 18.9 mmol) was added dropwise over 15 min to a solution of cubane[^{13}C]-carboxylic acid (1.23 g, 8.31 mmol) in 35 mL of dry diethyl ether at −70 °C. The resulting reddish-brown heterogenous mixture was stirred at −70 °C for 0.5 h and then at room temperature for 0.5 h. It was recooled to −70 °C and quenched with 5 mL of ACS grade acetone. The mixture was warmed to room temperature, diluted with CH_2Cl_2 (50 mL), washed with saturated aqueous $NaHCO_3$ (20 mL) and water (20 mL), dried over $MgSO_4$, and filtered. The solvents were carefully removed in vacuo on a rotary evaporator with bath temperature maintained below 30 °C to give 2.65 g of crude ketone. Crystallization from methanol gave 1.54 g of cubyl phenyl ketone (89%) as beige crystals. Further purification by vacuum sublimation gave colorless crystals: mp 110–111 °C; IR (CCl_4) ν 2988, 1664, 1325, 947 cm^{-1}; ^{1}H NMR δ 7.81 (m, 2 H), 7.52 (m, 1 H), 7.43 (m, 2 H), 4.46 (m, 3 H), 4.14 (m, 1 H), 4.09 ppm (m, 3 H); ^{13}C NMR δ 198.2 (enhanced), 134.9, 132.8, 128.6, 127.9, 63.1, 50.9, 47.0, 45.2 ppm.

Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octyl Phenyl [^{13}C]Ketone (*p*-Tolylsulfonyl)hydrazone (6). Cubyl phenyl [^{13}C]ketone (0.87 g, 4.2 mmol) and tosylhydrazide (0.86 g, 4.6 mmol) were dissolved separately in minimal portions of hot absolute ethanol. The solutions were combined and stirred at room temperature for 3 days. (Do not heat!) The solvents were removed in vacuo, and the residue was crystallized from methanol to give 1.37 g of cubyl phenyl ketone tosylhydrazone (87%) as a white powder: mp 152 °C dec; IR (CCl_4) ν 3285, 2994, 1598, 1160 cm^{-1}; ^{1}H NMR δ 7.79 (m, 2 H), 7.42 (m, 3 H), 7.31 (m, 3 H), 7.02 (m, 1 H), 4.10 (m, 3 H), 3.97 (m, 1 H), 3.86 (m, 3 H), 2.45 ppm (s, 3 H); ^{13}C NMR δ 156.5 (enhanced), 140.8, 135.4, 130.8, 129.6, 129.5, 129.4, 128.0, 60.3, 49.3, 48.1, 44.3, 21.6 ppm.

9-Ethoxy-1-phenyl[1-^{13}C]pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (7) and 9-Ethoxy-9-phenyl[9-^{13}C]pentacyclo-[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (8). Cubyl phenyl [^{13}C]ketone tosylhydrazone (97 mg, 0.26 mmol) was added to a solution of sodium ethoxide in ethanol prepared earlier from 71 mg (3.1 mmol) of sodium and 3 mL of absolute ethanol. The reaction mixture was heated to reflux for 5 h. The solvent was carefully removed in vacuo on a rotary evaporator with bath temperature maintained below 30 °C. The residue was taken up in 30 mL of CH_2Cl_2, and the solution washed with a saturated aqueous solution of $NaHCO_3$ (2 × 15 mL) and water (2 × 15 mL) and then dried over $MgSO_4$, filtered, and evaporated, leaving a brown oil. Column chromatography on Merck grade 60 silica gel (230–400 mesh) with 1:10 EtOAc/hexane gave a mixture of the title compounds as a light yellow oil. The ^{13}C NMR spectrum was consistent with published data.[2f] Enhancements were observed only at 101.7 and 61.0 ppm.

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Registry No. 1, 109719-29-1; 2, 109719-35-9; 4, 109719-34-8; 6, 124687-69-0; 7, 124687-70-3; 8, 124716-13-8; $Ba^{13}CO_3$, 51956-33-3; $^{13}CO_2$, 1111-72-4; pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane[^{13}C]carboxylic acid, 112043-88-6; iodocubane, 74725-77-2; cubylithium, 72507-56-3; pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octyl phenyl [^{13}C]ketone, 124687-68-9.

A General Procedure for the Selective Oxidation of Sulfides to Sulfoxides by Nitric Acid: Tetrabromoaurate(III) Catalyst in a Biphasic System

Francesco Gasparrini,* Mario Giovannoli, and Domenico Misiti

Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, P.le A. Moro 5, 00185 Roma, Italy

Giovanni Natile

Dipartimento Farmaco-Chimico, Via G. Amendola 173, 70126 Bari, Italy

Gianni Palmieri

Dipartimento di Scienze Chimiche, Via S. Agostino 1, 62032 Camerino, Italy

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Tetrabromoaurate(III) is an efficient catalyst for the oxidation of sulfides to sulfoxides by nitric acid in a biphasic system (nitromethane/water). The system is selective and can be applied to the oxidation of any type of dialkyl and alkyl aryl sulfide and also of diaryl sulfides activated by electron-releasing substituents. The nature of the active species has been investigated in relation to the mechanistic aspects.

Sulfoxides are gaining considerable interest as intermediates in organic synthesis and recent studies have been devoted to increasing the range of such compounds or improving their method of preparation.[1]

We have recently reported a procedure for the selective oxidation of dialkyl sulfides to the corresponding sulfoxides in a biphasic system using tetrabutylammonium tetrachloroaurate(III), $TBA^+AuCl_4^-$, as catalyst.[2,3] This procedure, however, was not applicable to the oxidation of hindered dialkyl sulfides, alkyl aryl sulfides, and diaryl sulfides, which required reaction times that were too long.

In an attempt to improve the above process, tetrabutylammonium tetrabromoaurate(III), $TBA^+AuBr_4^-$, has

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(2) Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; Palmieri, G. *Tetrahedron* **1983**, *39*, 3181.

(3) Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; Palmieri, G. *Tetrahedron* **1984**, *40*, 165.

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