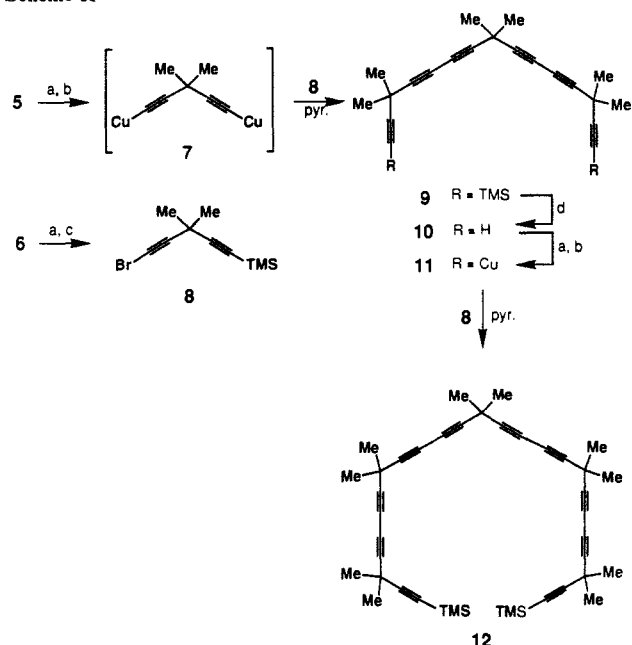


Scheme II<sup>a</sup>

<sup>a</sup>(a) *n*-BuLi, THF, 0 °C. (b) CuCl, 0 °C. (c) TsBr, -78 to 25 °C. (d) KOH, MeOH.

monomer (5) and to a hemi-protected derivative thereof (6).

Conversion of 5 to the bis(copper acetylide) 7 and of 6 to the bromoacetylide 8, as shown in Scheme II, followed by Cadiot-Chodkiewicz coupling gave the protected acyclic trimer 9 in 42% yield.<sup>8</sup> Cleavage of the trimethylsilyl groups from 9 released 10 (76%), which could then be cyclized to the closed trimer 1 in 30% yield under high-dilution conditions similar to those used in eq 1.<sup>9</sup> Alternatively, homologation of 10 at both ends, again with bromoacetylide 8, as shown in Scheme II, gave the protected acyclic pentamer 12 in 45% yield. After cleavage of the trimethylsilyl groups from 12 (63%), cyclization as in eq 1 gave the 25-membered-ring pentamer in 89% yield.<sup>10</sup> Completely analogous chemistry, starting from the symmetrically coupled dimer of 6, afforded the cyclic tetramer (2) and the cyclic hexamer (4).

The longest wavelength maximum in the UV absorption spectrum of the cyclic pentamer (3) appears at 259 nm, whereas the corresponding absorption in the spectrum of the cyclic trimer (1) appears as a shoulder at 277 nm (Table I and Figure 1). We believe this bathochromic shift to be a manifestation of significantly enhanced homoconjugation in 1 relative to that in 3, as discussed above, and not of geometric distortion of the diyne chromophore. Other 1,3-diyne which, according to molecular mechanics calculations, are bent out of linearity to about the same extent as those in 1 but lack homoconjugation have long wavelength absorption maxima at only 256 nm.<sup>11</sup> The cyclic tetramer (2) and the cyclic hexamer (4) exhibit UV spectra very similar to that of the cyclic pentamer (3, Table I).

In conclusion, we have found that cyclic homoconjugated polydiynes 1-4 are easy to construct, simple to handle in the laboratory, and convenient to study by UV absorption spectroscopy. The smallest member of the series (1) appears to be significantly more strongly homoconjugated than its larger homologues. We are continuing to study these compounds as well as a variety of mixed acetylene-diyne macrocycles.

(8) CAUTION! Copper acetylides and some bromoacetylides are potentially explosive when dry; it is safest never to remove solvent completely.

(9) A 30% yield of 1 was obtained by employing a mixture of Cu(OAc)<sub>2</sub> and CuCl at 60 °C for 3.5 h. The Breslow cyclization conditions<sup>7</sup> gave 1 in only 12% yield.

(10) The Breslow cyclization conditions<sup>7</sup> were employed for this cyclization.

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**Acknowledgment.** We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

**Registry No.** 1, 126191-37-5; 2, 126191-38-6; 3, 126191-39-7; 4, 126191-40-0; 5, 62496-43-9; 6, 4246-40-6; 6 (dimer), 126191-45-5; 8, 126191-41-1; 9, 126191-42-2; 10, 126216-28-2; 12, 126191-43-3; ClC(CH<sub>3</sub>)<sub>2</sub>C≡CTMS, 18387-63-8; BrMgC≡CTMS, 61210-52-4; HC≡C-[C(CH<sub>3</sub>)<sub>2</sub>C≡CC≡C]<sub>4</sub>C(CH<sub>3</sub>)<sub>2</sub>C≡CH, 126191-44-4.

## Automerization of Homocubylidene: Proof of a Reversible Olefin/Carbene Rearrangement

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Received December 18, 1989

Eaton and Hoffmann found that decomposition of cubyl-phenyldiazomethane gives 9-phenylhomocub-1(9)-ene (1) and discovered that this extremely twisted, anti-Bredt olefin rearranges to 1-phenylhomocubylidene (2), a singlet carbene.<sup>1</sup> Jones and Chen reported thereafter similar behavior for the desphenyl compound.<sup>2</sup> Herein we demonstrate that such extraordinary olefin-to-carbene rearrangements are reversible.<sup>3</sup>

We now know that the thermal decompositions of cubyl phenyl ketone tosylhydrazone (3) and of 1-phenylhomocubanone tosylhydrazone (4) in refluxing ethanolic sodium ethoxide give the identical distribution of ethyl ethers (Scheme I). As entry into the reaction from the "olefin side" (i.e., from 3) gives the same product distribution as entry from the "carbene side" (i.e., from 4), the reaction manifold would seem to allow for homocubene 1 and homocubylidene 2 to come into equilibrium. However, 2 might not be formed *directly* from the salt of 4.<sup>2,3</sup> Carbon migration could proceed concomitantly with loss of dinitrogen (Scheme II); this would give 1 without the intervention of 2, which would arise only subsequently from 1. Under this less-than-simple circumstance, the observation of an identical product ratio from the decompositions of 3 and 4 does not require that equilibrium be reached between the olefin and the carbene, nor even that these be interconvertible. We demonstrate now that at least the latter does in fact pertain.

For unambiguous proof of the interconversion, an unequivocal source of homocubylidene is needed.<sup>4</sup> We use here 1(9)-homocubene itself (Scheme III: the atom numbering is of independent structures and is not meant to correlate atoms).

Eaton and White have shown that the rearrangement of olefin 1 to carbene 2 proceeds by a shift of C<sub>2</sub> (or C<sub>8</sub>) from C<sub>1</sub> to C<sub>9</sub>, rather than by phenyl migration (see Scheme I).<sup>5,6</sup> If 1(9)-homocubene (5) were to rearrange to homocubylidene (6) in the same way (as will be demonstrated), then *in the reverse reaction*, homocubylidene to 1(9)-homocubene, if it does occur, any one of four identical cage carbons (C<sub>2</sub>, C<sub>5</sub>, C<sub>7</sub>, C<sub>8</sub>) could shift to C<sub>9</sub> (homocubylidene numbering). Were the original precursor labeled

(1) Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* 1987, 109, 5285. See also footnotes 13, 14, and 15 therein as well as the following: (a) Barton, T. J.; Yeh, M.-H. *Tetrahedron Lett.* 1987, 51, 6421. (b) Conlin, R. T.; Huffaker, H. B.; Kwak, Y.-W. *J. Am. Chem. Soc.* 1985, 107, 731. (c) Halton, B.; Bridle, J. H.; Lovett, E. G. *Tetrahedron Lett.* 1990, 31, 1313.

(2) Jones, M., Jr.; Chen, N. *J. Phys. Org. Chem.* 1988, 1, 305.

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(4) Cf. with refs 2 and 3.

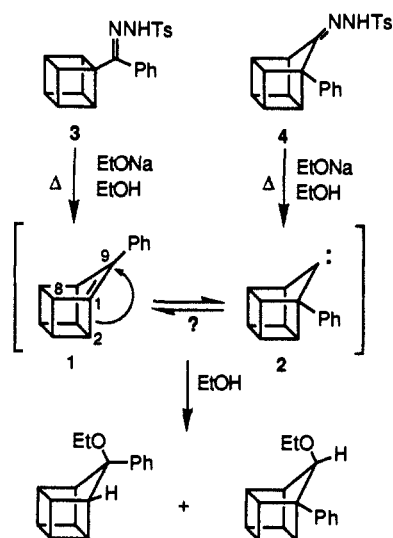
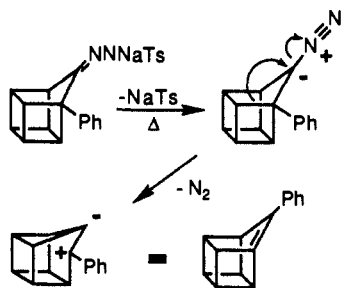
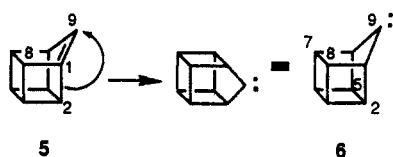
(5) Eaton, P. E.; White, A. *J. Org. Chem.* 1990, 55, 1321.

(6) Scrambling of carbon-bearing-phenyl about the cage does not occur significantly. Presumably the phenyl group biases the rearrangement of carbene 2 such that 1 is always formed. This is sensible as 1 is stabilized by conjugation.

**Table I.** Experimental (and Calculated) Distribution of  $^{13}\text{C}$  Label into the Products Obtained on Trapping of Homocubylidene under Various Conditions

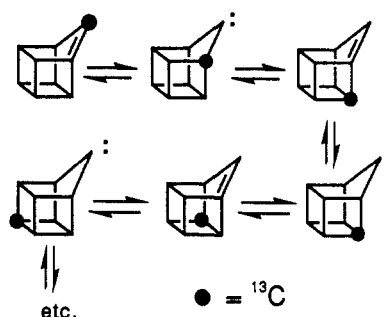
trap <sup>a</sup>	concn	product	% yield <sup>c</sup>	% label distribution by position <sup>d</sup>				$K_8/K_7^f$
				9	1, 6	2, 5, 7, 8	3, 4	
benzene	neat	8	75	0	89.7 (89.1)	10.3 (10.1)	<0.1 (0.3)	0.23
perfluorobenzene	neat	9	73	0	86.6 (86.6)	13.1 (13.0)	0.3 (0.5)	0.30
cyclohexane	neat	10	40	0	86.2 (86.2)	13.4 (13.3)	0.4 (0.5)	0.31
benzene	10 <sup>b</sup>	8	24	0	80.3 (80.3)	18.9 (18.6)	0.8 (1.1)	0.47
cyclohexane	10 <sup>b</sup>	10	33	0	78.9 (78.9)	20.1 (19.8)	1.0 (1.3)	0.51
cyclohexane	1 <sup>b</sup>	10	13	0	70.3 (70.3)	27.1 (27.1)	2.6 (2.6)	0.78
cyclohexane	0.1 <sup>b</sup>	10	4	0	62.1 (62.1)	32.7 (33.4)	5.2 (4.5)	1.11

<sup>a</sup>At reflux. <sup>b</sup>Volume % in  $\text{C}_6\text{F}_{14}$ . <sup>c</sup>Isolated and purified. <sup>d</sup>Calculated values in parentheses. <sup>e</sup>See text for definition. <sup>f</sup>Chosen to best fit calculated and observed label distribution.

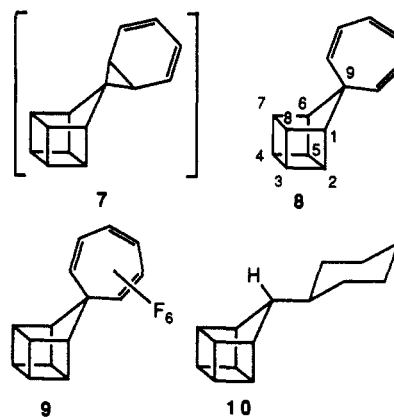
**Scheme I****Scheme II****Scheme III**

appropriately, the combination of these interconversions would lead ultimately to a homocubylidene in which the label was distributed about the cage methine positions (Scheme IV).

Decomposition in refluxing benzene of the sodium salt of the tosylhydrazone of cubanecarbaldehyde, 99%  $^{13}\text{C}$ -labeled, gives 9-spirohomo-cubantropyliene (8), formed via homocubylidene cyclopropanation of the solvent and subsequent opening of the product norcaradiene 7. Decomposition in refluxing hexafluorobenzene gives 9 similarly. Decomposition in boiling cy-

**Scheme IV**

clohexane produces 9-cyclohexylhomocubane (10) by insertion of the carbene into a cyclohexane C-H bond.



Close inspection of the  $^{13}\text{C}$  NMR spectrum of 8 showed no  $^{13}\text{C}$  label at the spiro carbon above natural abundance. This must mean that rearrangement of homocubene to homocubylidene occurs by carbon migration ( $\text{C}_2$  or  $\text{C}_8$  from  $\text{C}_1$  to  $\text{C}_9$ , olefin numbering), just as it does in the phenyl case. Had  $\text{C}_9$  of the olefin, which must initially have had all the label, become the carbene carbon by hydrogen migration, the spiro carbon in 8 would have been heavily labeled. Instead, only carbons 1(6) and 2(5,7,8) are significantly labeled.<sup>7</sup> The "wandering" of the label can only arise via automerization of homocubylidene. As there is no rational mechanism for this carbene-to-carbene rearrangement without the intermediacy of 1(9)-homocubene, the olefin-to-carbene rearrangement *must be reversible*.

When poorer carbene traps were used, thus allowing time for more automerizations, movement of the label through the skeleton

(7) Distributions were determined by integration of inverse gated decoupled FT  $^{13}\text{C}$  NMR spectra. Long delay times were used (100 s for 8 and 9, 25 s for 10). Integrals were corrected for  $^{13}\text{C}$  natural abundance by using the intensity of non-homocubyl carbon signals as reference.

was more pronounced. Dilution of the trap with an inert solvent (perfluorohexane) enhanced this further. The results are shown in Table 1. Automerization is not fast enough to provide for complete scrambling of the label [25:50:25 for positions 1(6), 2(5,7,8), and 3(4), respectively] before the reactive intermediates are destroyed in effectively irreversible reactions. The data, however, fit very well a statistical analysis correlating label distribution with the ratio of rate of automerization ( $K_a$ ) to rate of irreversible removal of the carbene ( $K_r$ ).<sup>8</sup>

Our findings provide unambiguous proof for automerization of homocubylidene and its corollary that the homocubene-to-homocubylidene rearrangement is indeed reversible. As the energy difference between 9-phenyl-1(9)-homocubene (1) and 1-phenylhomocubylidene (2) is less than that between the desphenyl pair,<sup>6,9</sup> it is economic to assume similar conclusions for this system.

**Acknowledgment.** This work was supported by the National Institutes of Health (GM 36436) and the Office of Naval Research. ONR provided in addition funding for the Varian VXR-400 NMR spectrometer essential to the project. R.B.A. acknowledges fellowship support from the NIH Pharmacological Sciences Training Program at The University of Chicago (GM 07151-14). We are most grateful to Professor Martin Saunders of Yale for his statistical analysis of the label-scrambling process.

(8) Saunders, M., private communication.

(9) Reference 1; footnote 12.

## Hydrocarbon Oxidation by Antimony Pentafluoride

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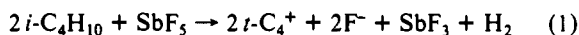
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Received November 21, 1989

Acid-catalyzed hydrocarbon conversion processes such as isomerization, alkylation, and cracking are industrial transformations of high economic importance. The common key step in these reactions is the formation of the reactive trivalent carbocations. Whereas a consensus has been reached on the nature of this intermediate species, the mode of its formation remains controversial despite the important contributions of mechanistic and structural studies facilitated by the use of superacid solutions as pioneered by Olah and his group.<sup>1</sup>

In this work, we report experimental proof of the direct oxidation of isobutane by antimony pentafluoride to the *tert*-butyl cation. The presence of a proton trap shows that the proton is not essential for this ionization process.

When isobutane (13.4 mmol) is mixed at  $-80^\circ\text{C}$  with excess  $\text{SbF}_5$  (65 mmol) in  $\text{SO}_2\text{ClF}$  (70 mmol) at  $-80^\circ\text{C}$  and the temperature is raised to  $-30^\circ\text{C}$ , a stoichiometric volume of hydrogen gas (6.5 mmol) can be collected over a period of 1 h. The quantitative transformation of isobutane into the *tert*-butyl ion is shown by  $^1\text{H}$  NMR spectra of the starting and resulting solutions. The reduction of  $\text{SbF}_5$  to  $\text{SbF}_3$  is evidenced by RX analysis of the white precipitate that occurs during the reaction, which can be written as



In fact,  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$  is a polymeric chain and the fluoride ions will be complexed and form polymeric  $\text{Sb}_n\text{F}_{5n+1}^-$  ions<sup>2</sup> ( $n = 4$  or 5).

When under the same experimental conditions excess acetone (molar ratio 3:1 to isobutane) is dissolved in the  $\text{SbF}_5\text{-SO}_2\text{ClF}$  solution before isobutane addition, only traces of hydrogen are detected, whereas the  $^1\text{H}$  NMR spectrum shows the complete ionization of isobutane to the *tert*-butyl ion and the formation of the corresponding amount of protonated acetone ( $\text{COH}^+$  signal at 13.5 ppm).

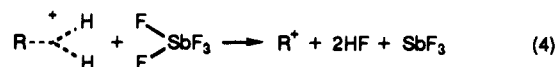
The ionization reaction of isobutane can thus be written as  $i\text{-C}_4\text{H}_{10} + 3\text{SbF}_5 + (\text{CH}_3)_2\text{CO} \rightarrow t\text{-C}_4\text{H}_9^+ + (\text{CH}_3)_2\text{COH}^+ + 2\text{SbF}_6^- + \text{SbF}_3$  (2)

In fact, as shown by the  $^1\text{H}$  chemical shift of the methyl groups of acetone ( $\delta = 3.0$  ppm) and in accord with the literature on  $\text{SbCl}_5$  adducts,<sup>3</sup> the ketone is not a free base in the presence of  $\text{SbF}_5$  but complexed by the Lewis acid at the start. The immediate appearance of the  $\text{COH}^+$  signal during the ionization process of isobutane shows, however, that the affinity for the proton is much higher. Since the early observations of alkane ionization in superacid solutions reported by Olah and his group,<sup>4</sup> a large number of attempts have been made to establish the mechanism of the ionization step. The first mechanism as proposed by Olah<sup>5</sup> is based on the  $\sigma$ -donor ability of the C-H and C-C bonds. The ionization step occurs after protonation of the alkane via a three-center two-electron bond intermediate with formation of hydrogen:

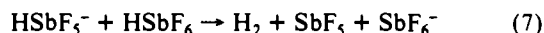
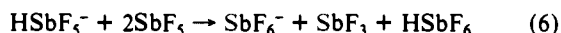
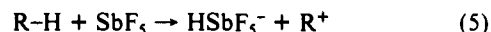


This pathway has been strongly supported by experiment<sup>6</sup> as well as theory<sup>7</sup> and thermodynamics.<sup>8</sup> The potential acidity diagrams (Pourbaix type) of the lower alkanes plotted vs the  $\text{H}^+/\text{H}_2$  system as shown by Devynck<sup>9</sup> can be very useful to illustrate the acidity domain in which this reaction will take place. However, whereas the stoichiometric production of hydrogen could be demonstrated in various systems, this was not always the case, and the deficiency in  $\text{H}_2$  was related to the concomitant reduction of  $\text{SbF}_5$ .<sup>10-12</sup> For this reason, controversial propositions have been made in which  $\text{SbF}_5$  was the main oxidant.

As  $\text{SbF}_5$  is not reduced by  $\text{H}_2$  under the usual experimental conditions, two different mechanistic pathways have been proposed implying the participation of the Lewis acid in the ionization process: (1) reduction of  $\text{SbF}_5$  by the protonated alkane (reaction 4), which is a way to attribute the reduction of  $\text{SbF}_5$  to an activated



form of hydrogen as proposed by Olah<sup>11</sup> and later by Ledford;<sup>12</sup> and (2) reduction of  $\text{SbF}_5$  after formation of an antimony hydride obtained by hydride abstraction from the alkane (reactions 5-7).



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