

## References and Notes

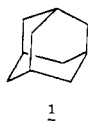
- (1) Several terms have been applied to such a process, e.g., symmetrization of reactivity,<sup>2</sup> charge affinity inversion,<sup>3</sup> and umpolung.<sup>4</sup>
- (2) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).
- (3) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
- (4) D. Seebach and M. Kolb, *Chem. Ind. (London)*, 687 (1974).
- (5) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969).
- (6) B. Gröbel and D. Seebach, *Synthesis*, 357 (1977).
- (7) D. Seebach and D. Enders, *Angew. Chem., Int. Ed. Engl.*, **14**, 15 (1975).
- (8) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **16**, 339 (1977), and D. Hoppe, *ibid.*, **13**, 789 (1974).
- (9) For another approach to primary amine activation, see R. Schlecker and D. Seebach, *Helv. Chim. Acta*, **60**, 1459 (1977).
- (10) A. Michaelis and O. Störbeck, *Justus Liebig's Ann. Chem.*, **274**, 187 (1893).
- (11) (a) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149 (1967). (b) G. Kresze and W. Wucherpfennig in "Newer Methods of Preparative Organic Chemistry", Vol. 5, W. Foerst, Ed., Academic Press, New York, N.Y., 1968, p. 109.
- (12) D. Klamann, C. Sass, and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959).
- (13) Distillation of *N*-sulfinylamines should be carried out at oil-bath temperatures below ~150 °C; vigorous decomposition has been observed at higher temperatures. Similar thermal instability has been observed with *N*-sulfinylsulfonamides<sup>11b</sup> and *N*-sulfinylbenzamide.<sup>14</sup>
- (14) O. Tsuge and S. Mataka, *Bull. Chem. Soc. Jpn.*, **44**, 2836 (1971).
- (15) This is in good agreement with the chemical shift of 42.7 ppm reported by House<sup>16</sup> for the allylic methylene in aldehyde **6** (NHBz=CHO), whereas the chemical shift of the axial methylene in its epimer is 34.6 ppm.
- (16) H. O. House, J. Lubinkowski, and J. J. Good, *J. Org. Chem.*, **40**, 86 (1975).

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 Received November 14, 1977

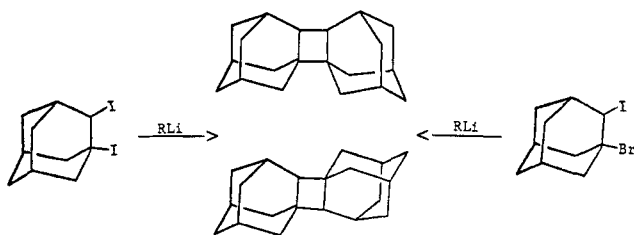
### Adamantene by Ring Enlargement of 3-Noradamantylcarbene<sup>1</sup>

Sir:

The last 5 years have seen an intensive expansion of the attempt in 1960 by Montgomery and Roberts<sup>2</sup> to synthesize the bridgehead olefin, adamantene<sup>3-13</sup> (**1**). These efforts reveal not only the intrinsic interest of this molecule and its reactions, but reflect as well a continuing controversy over the properties of **1** observed in the various modes of generation.



Although several attempts to make adamantene have ended in failure,<sup>2-6</sup> two groups reported in 1972 the isolation of dimers of the formula C<sub>20</sub>H<sub>28</sub> from the treatment of either, 1,2-diiodoadamantane<sup>7</sup> or 1-bromo-2-iodoadamantane<sup>8</sup> with

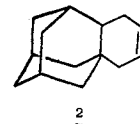


butyllithium. The dimers, which were formed in remarkably high yield (80–98%), were quite reasonably assigned the structures appropriate for the cyclobutanes formed by [2 + 2] dimerization of **1**.<sup>8b</sup> It was specifically noted that furan was a totally ineffective trap for **1**, as no Diels–Alder adduct could be isolated.<sup>7,8</sup>

Two different routes were published the next year. Adamantene, produced by the photolysis of 1- or 2-adamantylphenylacetate,<sup>9</sup> was trapped in methanol to yield 1-methoxyadamantane. In addition, Wynberg and co-workers heated

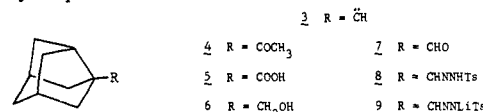
adamantane 1,2-di-*tert*-butyl perester to 70 °C in dimethylfuran and isolated 9% Diels–Alder adduct.<sup>10</sup> Moreover, no dimers were found. The classic test for an intermediate is the obtention of the same products from different modes of generation. Since the diperester and the dihaloadamantane–butyllithium products were not at all the same, it seemed unlikely (granting the difference in reaction conditions) that the same “adamantene” was formed by both routes.

An adduct (**2**), although from butadiene rather than from



furan, was isolated by McKervey and co-workers in 1974;<sup>11</sup> substantial amounts of **2** are formed by treatment of 1,2-diiodoadamantane with butyllithium<sup>12</sup> or with lithium diphenylphosphide<sup>13</sup> in neat butadiene. Once more no adduct with dimethylfuran could be found.<sup>13</sup>

Thus the picture remains clouded. As Wynberg et al. note,<sup>10</sup> it is conceivable that dimer formation from 1,2-dihaloadamantane does not involve adamantene. The facile coupling of 1- and 2-haloadamantane when treated with alkylolithium<sup>14,15</sup> raises the possibility of similar processes operating in dimer formation and perhaps even in the formation of **2**. Wynberg's isolation of an adduct with dimethylfuran could also be misleading, as stepwise processes are not impossible in this reaction, either. We present in this paper evidence that adamantene, formed by a new route, the ring expansion of carbene **3** in the gas phase, possesses properties different from those previously implied.

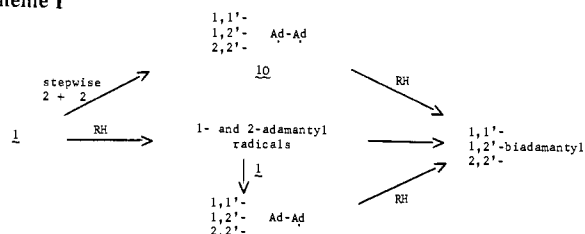


Carbene **3** was chosen as precursor for **1** because we had previously demonstrated that such ring-expansion reactions were capable of generating compounds containing bridgehead double bonds in six-membered rings.<sup>16</sup> Moreover, formation of **1** was unlikely to be severely complicated by ring expansion of the larger “wrong” bridge.<sup>16</sup> Clearly problems associated with organometallic reagents were sure to be absent and we hoped, therefore, to be able to shed light upon the controversy surrounding the properties of **1**.

3-Noradamantyl methyl ketone (**4**)<sup>17</sup> yielded 3-noradamantanecarboxylic acid (**5**) on treatment with NaOBr (mp 105–108 °C; lit. 106–107,<sup>18</sup> 105–106,<sup>19</sup> 108–109 °C<sup>17</sup>). Reduction of **5** with LiAlH<sub>4</sub> gave the corresponding alcohol **6** (mp 144–145 °C; lit. 142–144 °C<sup>18</sup>) which could be oxidized to aldehyde **7** (mp 128–132 °C; lit. 130–133 °C<sup>20</sup>). Tosylhydrazone **8** (mp 128 °C dec)<sup>21</sup> yielded a salt **9** on treatment with butyllithium.

Flash vacuum pyrolysis of **9** at 300 °C in the apparatus described previously<sup>22</sup> led to four products, isolable by gas chromatography in 24% overall yield. These were 1,1'-biadamantyl (29.6%), 1,2'-biadamantyl (8.2%), 2,2'-biadamantyl (7.9%), and dimers of the formula C<sub>20</sub>H<sub>28</sub> (54.3%). The biadamantyls were synthesized independently<sup>12,14,15</sup> and the dimers compared to a sample provided by Professor McKervey.<sup>23</sup> Although the retention time of our dimers matched exactly that of the sample provided by Professor McKervey, there were small differences in the <sup>1</sup>H NMR spectra. This is not surprising, as one would not expect the same mixture of stereoisomers to be formed under our conditions and those of McKervey<sup>7</sup> or Lenoir.<sup>8</sup> The dimer formed in our reaction showed a band in the Raman spectrum (260 cm<sup>-1</sup>) comparable with that reported by Kovacic<sup>24</sup> and attributed to the cyclobutane ring. When **9** is decomposed in a flow system with bu-

Scheme I



tadiene, the same four products are accompanied by 13% **2**. The structure of **2** was verified by a comparison of spectra with those obtained by McKervery.<sup>12,23</sup> In addition, 5% of another product, whose spectra were consistent with a vinylcyclobutane, was isolated. Although the detailed structure of this compound awaits further work, it appears to be the result of a [2 + 2] cycloaddition of **1** to butadiene.

It seems clear from the formation of **2** that adamantene is produced by the pyrolysis of **9**. Formation of the C<sub>20</sub>H<sub>28</sub> fraction is less diagnostic, as it is difficult to resolve fully the question of the composition of this mixture. At least isolation of this material is consistent with the intermediacy of adamantene. Most intriguing is the isolation of the biadamantyls. What is the mechanism of their formation? Control experiments show that they are not secondary products formed by pyrolysis of the C<sub>20</sub>H<sub>28</sub> fraction and do not interconvert under the reaction conditions. Three possible routes suggest themselves (Scheme I). Were adamantene to dimerize in a stepwise fashion, a set of 1,4 diradicals **10** would be produced that might abstract hydrogen to form the biadamantyls. However, we know of no precedent for such a process. If adamantene abstracts hydrogen to give the 1- and 2-adamantyl radicals, either subsequent dimerization or addition to adamantene would yield the biadamantyls.<sup>25</sup>

No source of biadamantyls not involving adamantene, probably a powerful hydrogen abstractor, is apparent. If this surmise is correct, why haven't biadamantyls been formed in all the previously reported reactions thought to involve adamantene? If adamantene is an intermediate in all these reactions, the difference in behavior may be due to the disparate environments or even to the possibility that adamantenes of different spin states, singlet or triplet, are involved.

## References and Notes

- (1) We thank the National Science Foundation for generous support of this work through Grant MPS 74-05690.
- (2) J. D. Roberts and L. K. Montgomery, *J. Am. Chem. Soc.*, **82**, 4750 (1960).
- (3) B. L. Adams, J.-H. Liu, and P. Kovacic, *Tetrahedron Lett.*, 427 (1974).
- (4) J. L. Fry, M. G. Adlington, R. C. Badger, and S. K. McCullough, *Tetrahedron Lett.*, 429 (1974).
- (5) R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 4752 (1970); R. B. Gagosian, J. C. Dalton, and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 5189 (1975).
- (6) R. R. Sauers, M. Gorodetsky, J. A. Whittle, and C. K. Hu, *J. Am. Chem. Soc.*, **93**, 5520 (1971).
- (7) D. Grant, M. A. McKervery, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972).
- (8) (a) D. Lenoir, *Tetrahedron Lett.*, 4049 (1972); (b) D. Lenoir and J. Firl, *Justus Liebig's Ann. Chem.*, 1467 (1974).
- (9) J. E. Gano and L. Eizenberg, *J. Am. Chem. Soc.*, **95**, 972 (1973).
- (10) A. H. Alberts, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 3047 (1973).
- (11) W. Burns and M. A. McKervery, *J. Chem. Soc., Chem. Commun.*, 858 (1974).
- (12) W. Burns, D. Grant, M. A. McKervery, and G. Step, *J. Chem. Soc., Perkin Trans. 1*, 234 (1976).
- (13) D. G. Gillespie and B. J. Walker, *Tetrahedron Lett.*, 1673 (1977).
- (14) P. T. Lansbury and J. D. Sidler, *Chem. Commun.*, 373 (1965).
- (15) J. A. van Zorge, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, **89**, 781 (1970); J. H. Wieringa, H. Wynberg, and J. Strating, *Synth. Commun.*, **1**, 7 (1971). The relative thermodynamic stabilities of the three biadamantyls have been determined by direct equilibration: J. Slutsky, E. M. Engler, and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.*, 685 (1973).
- (16) A. D. Wolf and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 8209 (1973); M. Farcaşiu, D. Farcaşiu, R. T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8207 (1973); E. Wiscott and P. v. R. Schleyer, *Tetrahedron Lett.*, 2845 (1967).

- (17) R. M. Black and G. B. Gill, *Chem. Commun.*, 972 (1970).
- (18) B. R. Vogt and J. R. E. Hoover, *Tetrahedron Lett.*, 2841 (1967).
- (19) H. Stetter, H. G. Thomas, and K. Meyer, *Chem. Ber.*, **103**, 863 (1970).
- (20) B. L. Adams and P. Kovacic, *J. Am. Chem. Soc.*, **97**, 2829 (1975).
- (21) This new compound gave a satisfactory elemental analysis.
- (22) W. Ando, A. Sekiguchi, A. J. Rothschild, R. R. Gallucci, M. Jones, Jr., T. J. Barton, and J. A. Kilgour, *J. Am. Chem. Soc.*, **99**, 6995 (1977).
- (23) Professor McKervery has been most helpful in providing samples and spectra. We are very grateful for his assistance.
- (24) B. L. Adams and P. Kovacic, *J. Am. Chem. Soc.*, **96**, 7014 (1974).
- (25) The source of hydrogen is unknown. However, in other systems we have determined that it is not the methyl of the tosyl group. G. R. Chambers, unpublished work.

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Received October 25, 1977

## Ab Initio Studies of the Metal-Metal Bond in Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup>

Sir:

Since the discovery<sup>1,2</sup> of the "quadruple" metal-metal bond in Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup>, numerous experimental<sup>3-6</sup> and theoretical<sup>7-9</sup> studies have been carried out to understand the bonding and electronic spectra of this species and related complexes. In this preliminary communication we report the results of ab initio calculations on the lowest electronic states of Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> and Re<sub>2</sub>Cl<sub>8</sub><sup>3-</sup>. These calculations have been made possible by the development of ab initio effective core potentials<sup>10</sup> (ECP's) which enable one to replace all but the outer valence electrons with a local potential which reproduces the energies and shapes of the valence orbitals. Calculations using ECP's yield results which are generally in good agreement with all-electron calculations. In addition, the dominant relativistic effects in heavy atoms such as Re can be included<sup>11</sup> in the ECP's. Although an assessment of the overall reliability of core potential calculations will await results of many more calculations, recent studies of Au, Hg and Xe compounds<sup>12</sup> yielded potential energy curves, excitation energies, and ionization potentials that compared well with experimental data.

Ab initio studies by Benard and Veillard<sup>13</sup> of multiple bonds in Cr dimers have shown that a proper description requires a multi-configuration wavefunction, in contrast to the traditional single-configuration Hartree-Fock wavefunction.<sup>14</sup> These effects of electron correlation can account for as much as 100-200 kcal/mol of the bond energy in Cr and Mo dimers,<sup>13,15</sup> and for ~90 kcal/mol of the triple bond in N<sub>2</sub>.<sup>16</sup> The starting point for the present calculations on Re<sub>2</sub>Cl<sub>8</sub><sup>2-</sup> is a generalized valence bond (GVB) description<sup>16,17</sup> of the eight electrons in the Re-Re bond while the remaining Cl-like orbitals are described in terms of doubly-occupied molecular orbitals. Instead of representing the overall wavefunction by the single configuration ( . . . (σ)<sup>2</sup>(π<sub>x</sub>)<sup>2</sup>(π<sub>y</sub>)<sup>2</sup>(δ<sub>xy</sub>)<sup>2</sup>) each of the pairs in the Re-Re bond is represented by a two-configuration function (e.g., c<sub>1</sub>(σ)<sup>2</sup> - c<sub>2</sub>(σ\*)<sup>2</sup> instead of (σ)<sup>2</sup>, where σ(σ\*) is the bonding (antibonding) combination of metal 5d<sub>z<sup>2</sup></sub>-like orbitals). This allows proper dissociation into ReCl<sub>4</sub><sup>-</sup> fragments (when c<sub>1</sub> = c<sub>2</sub> for all four pairs). Alternatively each pair can be cast into a GVB representation (e.g., σ<sub>a</sub>(1)σ<sub>b</sub>(2) + σ<sub>b</sub>(1)σ<sub>a</sub>(2) for the σ pair) where the overlap of the GVB orbitals (σ<sub>a</sub>|σ<sub>b</sub>) = S<sub>σ</sub> = (c<sub>1</sub> - c<sub>2</sub>)/(c<sub>1</sub> + c<sub>2</sub>) can be taken to be a measure of the bond order. A single contracted Gaussian function was used to represent the 3s and 3p functions on each