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# Novel cycloaddition of dimethylacetylene to the dimethylacetylene radical cation: Direct observation by ESR

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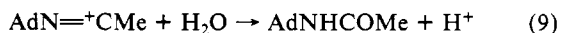
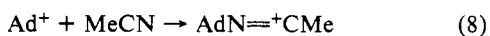
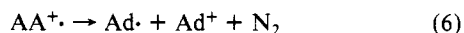
**Table I.** Products of Reaction of Thianthrene Cation Radical Perchlorate with 1,1'-Azoadamantane in Acetonitrile<sup>a</sup>

| reactants <sup>b</sup> |                                                | products <sup>b</sup> |                   |                     |                    |                   |                   |                               |
|------------------------|------------------------------------------------|-----------------------|-------------------|---------------------|--------------------|-------------------|-------------------|-------------------------------|
| AA                     | Th <sup>+</sup> ·ClO <sub>4</sub> <sup>-</sup> | AdNHCOMe <sup>c</sup> | AdOH <sup>d</sup> | AdCOMe <sup>d</sup> | AdH <sup>d</sup>   | AdAd <sup>c</sup> | Th <sup>e,h</sup> | N <sub>2</sub> <sup>c,i</sup> |
| 0.459                  | 0.815                                          | 0.752                 |                   |                     |                    | 0.011             | 0.822             |                               |
| 0.566                  | 1.00                                           | 1.02 <sup>e</sup>     | 0.0034            | 0.031 <sup>f</sup>  | 0.001 <sup>g</sup> | 0.014             |                   |                               |
| 0.051                  | 0.050                                          |                       |                   |                     |                    |                   |                   | 0.0367                        |
| 0.051                  | 0.050                                          |                       |                   |                     |                    |                   |                   | 0.0398                        |
| 0.027                  | 0.0505                                         |                       |                   |                     |                    |                   |                   | 0.0273                        |

<sup>a</sup> Distilled over P<sub>2</sub>O<sub>5</sub>. <sup>b</sup> In mmol. <sup>c</sup> Isolated yield. <sup>d</sup> GC assay, SE-30 capillary column, with naphthalene as an internal standard. <sup>e</sup> Isolated as the perchloric acid salt, amounting to 90% of the AA. The difference between this and the first entry (amounting to 81.9% of AA) represents losses in the extractive isolation of AdNHCOMe. <sup>f</sup> This represents 5.5% of the AA. Measurements in two other separate experiments gave 5.7% and 5.9% of the AA. <sup>g</sup> This represents 0.2% of the AA. <sup>h</sup> A small amount of thianthrene 5-oxide (ThO) was also obtained. <sup>i</sup> N<sub>2</sub> was measured by conventional vacuum-line. Toepler-pump techniques. In these cases, solid Th<sup>+</sup>·ClO<sub>4</sub><sup>-</sup> and AA were placed in separate arms of a Y-tube, to each of which approximately 1 mL of acetonitrile was added. Reactants were mixed after customary freeze-thaw degassing and sealing.

or that very few free Ad· are formed. Such free Ad· that are produced mainly add to the nitrile carbon<sup>18</sup> rather than abstracting hydrogen from MeCN. In support of the possibly facile oxidation of Ad·, it should be noted that the ionization potential (IP) of Th is near 7.90 eV,<sup>19,20</sup> while the IP of Ad· should be similar to the 6.9 eV found for *tert*-butyl radical.<sup>21</sup> Moreover, Th has a higher oxidation potential (1.3 V) than Fe(phen)<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub> (0.99 V) but even the latter oxidizes *tert*-butyl radical rapidly.<sup>9,22</sup>

The simplest representation of the reaction of Th<sup>+</sup>· with AA and the formation of so much AdNHCOMe is given in eq 5-9.



Azoalkane radical cations (eq 5 and 6) have not been investigated previously except for a recent photochemical study of bicyclic azoalkanes in CCl<sub>4</sub>.<sup>24</sup> Although many azoalkanes exhibit a molecular ion in mass spectrometry,<sup>25</sup> the irreversible nature of their cyclic voltammograms<sup>26</sup> is consistent with the postulated decomposition of AA<sup>+</sup>. If eq 5-9 were the sole reaction pathways, the stoichiometry of reaction would be 2.00:1.00 Th<sup>+</sup>·/AA. However, in each of seven measurements of the ratio of reactants, made by adding AA until the color of the Th<sup>+</sup>· disappeared, we obtained a molar ratio of 2.00:1.13 Th<sup>+</sup>·/AA. This ratio can be accommodated by the escape of adamantyl radicals from oxidation (eq 7) and their entering into some other reactions. In that case, more AA would be needed for electron transfer to remaining Th<sup>+</sup>· than required by reactions 5-7 and the ratio 2.00:1.00. The ratio found, 2.00:1.13, says that 88.5% of adamantyl groups were oxidized to Ad<sup>+</sup>, which corresponds well with the 91% yield of Ad<sup>+</sup>-derived products.

Although the major products are rationalized by eq 1-9, the origin of the 2.5% biadamantyl remains uncertain. One would not expect free Ad· to recombine because reaction with solvent is far more probable; moreover, AdAd continued to form in the

presence of BrCCl<sub>3</sub>. These considerations suggest that two Ad· are occasionally released in the same solvent cage, perhaps by decomposition of a complex of Th<sup>+</sup>· and AA. In that case, Th<sup>+</sup>· is regenerated and thus serves as a catalyst for the decomposition of AA into AdAd. Complexes of Th<sup>+</sup>· with nucleophiles have been identified kinetically by Parker and co-workers, e.g., with anisole.<sup>27</sup> The oxidation of AA by Th<sup>+</sup>· may involve such a complexation route.

In summary, a thermally stable azoalkane has been shown to undergo facile oxidative decomposition under mild conditions. The postulated intermediate, an azoalkane radical cation, has received scant attention previously, though the corresponding radical anions are known.<sup>28</sup> The new reaction described herein further expands the chemistry of the remarkably versatile azo linkage.<sup>29,30</sup>

**Registry No.** Th<sup>+</sup>·, 34507-27-2; Th<sup>+</sup>·ClO<sub>4</sub><sup>-</sup>, 21299-20-7; AA, 21245-62-5; Th, 92-85-3; AdNHCOMe, 880-52-4; AdH, 281-23-2; AdAd, 3732-31-8; AdNHCOMe·HClO<sub>4</sub>, 95532-46-0; AdN=CMe<sup>+</sup>, 95532-47-1; AdOH, 768-95-6; AdCO, 1660-04-4; acetonitrile, 75-05-8.

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### Novel Cycloaddition of Dimethylacetylene to the Dimethylacetylene Radical Cation: Direct Observation by ESR

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It has been well established that, for some aromatic and olefinic hydrocarbons,<sup>1</sup> the monomer radical cation reacts with the parent molecule to form the dimer cation with a sandwich structure. In contrast, we find a [1 + 2] cycloaddition of dimethylacetylene (DMA) radical cation to the parent molecule in solid Freon matrix at ca. 100 K. As far as we are aware, this is the first study in

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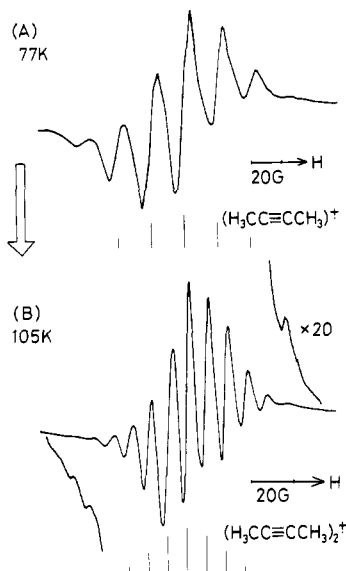
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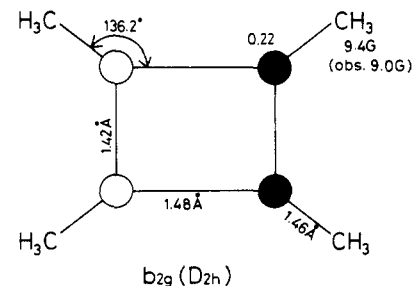


**Figure 1.** First-derivative ESR spectra of a  $\gamma$ -irradiated solid solution of ca. 0.3 mol % dimethylacetylene (DMA) in Freon-113 recorded at 77 (A) and 105 K (B): (A) the monomer radical cation,  $\text{CH}_3\text{C}\equiv\text{CCH}_3^+$  ( $\text{DMA}^+$ ); (B) tetramethylcyclobutadiene radical cation ( $\text{c-C}_4(\text{CH}_3)_4^+$ ) formed by a cycloaddition of the  $\text{DMA}^+$  to DMA.

which the cycloaddition reaction is initiated by a monomer radical cation as a precursor and has been clearly characterized by ESR spectroscopy.

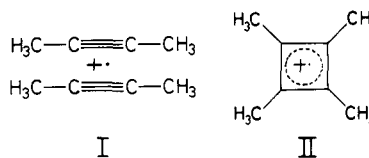
ESR spectrum shown in Figure 1A was observed for a  $\gamma$ -irradiated solid solution of ca. 0.3 mol % in Freon-113 ( $\text{CCl}_2\text{FC-ClF}_2$ ). The spectrum consists of seven hyperfine lines of  $a(6\text{ H}) = 21.6\text{ G}$  ( $g = 2.0057$ ).<sup>2,3</sup> An observation of six equivalent protons' hf coupling indicates that the spectrum observed is attributed to the monomer radical ion of DMA, not to the neutral radical. Judging from an ionization potential of DMA ( $\text{IP}_1 = 9.9\text{ eV}$ )<sup>4</sup> the ionic species responsible for the spectrum is, without doubt, the dimethylacetylene radical cation,  $\text{DMA}^+$ , which has been generated by a hole transfer from the matrix to the solute.<sup>5</sup> The spectrum observed at 4.2 K showed a broad and less resolved hf pattern. If the  $\text{DMA}^+$  retains a linear  $\text{C}_{3v}$  structure as the neutral DMA, it would be a  $^2\Pi$  radical and its orbital angular momentum would not be quenched. The momentum of the observed  $\text{DMA}^+$  is very efficiently quenched as evidenced in its  $g$  value (2.0059). Therefore, the  $\text{DMA}^+$  is expected to be distorted from the  $\text{C}_{3v}$  to have, probably, a bent planar structure due to a Jahn-Teller effect; it may be dynamically averaged between equivalent structures and/or undergoing restricted motions at 77 K, and less so at 4.2 K.

On annealing the sample to 105 K, the spectrum of  $\text{DMA}^+$  was irreversibly converted into that shown in Figure 1B, which consisted of 13 equally spaced lines of  $a(12\text{ H}) = 9.0\text{ G}$  ( $g = 2.0026$ ).<sup>2</sup> A possible radical species is either a symmetric sandwich



**Figure 2.** Experimental  $^1\text{H}$  hf splitting (value in parentheses) compared with the theoretical value calculated for the optimized  $D_{2h}$  structure by the INDO MO method, the SOMO being  $2b_{2g}$  in  $D_{2h}$ . The optimized geometrical parameters are given in the figure. The value of 0.22 refers to the calculated spin density in the carbon  $2p\pi$  orbital. The  $^1\text{H}$  hf splitting calculated is an average of the values obtained for various configurations of the methyl group, i.e., assuming the rotating methyl group.

type of dimer radical cation (I) or tetramethylcyclobutadiene ( $\text{c-C}_4(\text{CH}_3)_4$ ) radical cation (II). The hf splitting of radical I



is expected to be one-half that of the monomer radical, i.e., 10.8 G, which is 1.8 G larger than that observed. It is impossible to directly compare the observed spectrum in Figure 1B with that of species II which is prepared by a hole transfer to neutral  $\text{c-C}_4(\text{CH}_3)_4$  in the same matrix. The reason is that  $\text{c-C}_4(\text{CH}_3)_4$  is not available because of its unstable property.<sup>6</sup> However, Hogeveen et al.<sup>7</sup> have already observed an ESR spectrum of  $\text{c-C}_4(\text{CH}_3)_4^+$  formed by UV illumination to the  $\text{AlCl}_3$  complex of  $\text{c-C}_4(\text{CH}_3)_4$ <sup>8</sup> which was prepared by treating DMA with  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$ . The hf splitting reported for species II is  $a(12\text{ H}) = 8.7\text{ G}$ , which is very close to the observed value (9.0 G) in the present experiment. Therefore, it is reasonable to attribute spectrum in Figure 1B to species II which is formed by a  $[1 + 2]$  cycloaddition reaction of the monomer radical cation to the neutral molecule. When higher concentration of DMA (above ca. 5 mol %) was used in the experiments, the spectrum of II was already observed at 77 K together with that of the monomer radical cation.<sup>9</sup> This result suggests that the cycloaddition can be diffusion controlled and proceed with a small activation energy in the present solid matrix.

Upon further annealing of the sample to ca. 125 K, the radical cation of II was again irreversibly converted to a propargyl-type radical,  $\text{CH}_2=\text{C}\equiv\text{C}-\text{CH}_3$ ,<sup>10</sup> which was characterized by  $a_1(2\text{ H}) = 18.6\text{ G}$ ,  $a_2(3\text{ H}) = 12.5\text{ G}$ , and  $g = 2.0021$ . A possible mechanism to form this neutral radical is a ring opening of II, which is followed by a deprotonation. Taking into account the unstable property of cyclobutadiene ring,<sup>6</sup> it is consistent with assuming the species II, not I, as a precursor of the propargyl-type

(2) (a) Assignment of the both  $\text{DMA}^+$  and  $\text{c-C}_4(\text{CH}_3)_4^+$  has been further confirmed by observing the spectra of the corresponding isotopic species,  $\text{CH}_3\text{C}\equiv\text{CCD}_3^+$  and  $\text{c-C}_4(\text{CH}_3)_2(\text{CD}_3)_2^+$  (Shiotani, M.; Ohta, K.; Sohma, J.; Hasegawa, A.; Symons, M. C. R., to be published). (b) The obtained  $g$  and hf splittings have been determined by assuming the isotropic spectra, although the observed spectra (Figure 1A,B) show slightly asymmetric line shapes due to small  $g$  and hf anisotropies.

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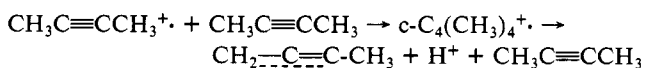
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(9) When Freon-114 ( $\text{CF}_2\text{ClCF}_2\text{Cl}$ ) was used instead of Freon-113, only the spectrum of II had been observed already at 77 K even for dilute DMA solution of ca. 0.05 mol %. On the other hand, for  $\text{SF}_6$  matrix, fluorine atom addition type of radicals have been observed (Shiotani, M.; Nagata, Y.; Sohma, J. *J. Phys. Chem.* **1982**, *86*, 4131).

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radical observed. The reactions detected are summarized as follows:



Similar ESR studies have been carried out on other substituted acetylenes such as methylacetylene, ethylacetylene, and diethylacetylene and tentative evidence has been obtained for the analogous cycloaddition of methylacetylene radical cation to methylacetylene.

Our INDO calculations<sup>11</sup> of  $\text{c-C}_4(\text{CH}_3)_4^\cdot$  resulted in a rectangle ( $D_{2h}$ ) structure at the optimized geometry where the semioccupied molecular orbital (SOMO) is  $b_{2g}$ , similarly to the ab initio calculations of cyclobutadiene.<sup>6</sup> The experimental proton hf splitting was favorably reproduced by the present calculations (cf. Figure 2). Assuming the sandwich structure I, any reasonable  $^1\text{H}$  hf splitting was not obtained by the calculations. These results further support a formation of  $\text{c-C}_4(\text{CH}_3)_4^\cdot$ . By employing the frontier orbital interaction scheme,<sup>12</sup> the cycloaddition can be represented in terms of the interaction of the SOMO of  $\text{DMA}^\cdot$  with the HOMO (highest occupied molecular orbital) of DMA. It should be noted that the concerted [2 + 2] suprafacial process is symmetry forbidden for the  $\pi-\pi^*$  DMA cycloaddition (i.e., HOMO-LUMO interaction). The analogous cycloaddition reaction, but initiated by the monomer radical anion, has been observed for tetrafluoroethylene in solid tetramethylsilane matrix by ESR spectroscopy:  $\text{C}_2\text{F}_4 + \text{C}_2\text{F}_4^\cdot \rightarrow \text{c-C}_4\text{F}_8^\cdot$ .<sup>13</sup>

**Acknowledgment.** This research has been partially supported by the Grant for Scientific Research of the Ministry of Education in Japan (Grant 59550602).

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### Asymmetric Synthesis of the Diastereomeric 1-(2-Cyclohexenyl)-1-alkanols in High Optical Purity via a Stereochemically Stable Allylic Borane, B-2-Cyclohexen-1-ylidiisopinocampheylborane

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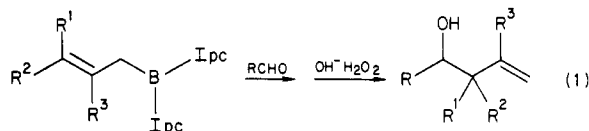
Revised Manuscript Received February 18, 1985

The hydroboration of 1,3-cyclohexadiene by (+)- and (-)-diisopinocampheylborane at  $-25^\circ\text{C}$  provides the enantiomeric B-2-cyclohexen-1-ylidiisopinocampheylboranes in 94% ee. These enantiomeric allylic boranes, the first such derivatives to be synthesized, retain their stereochemical identity under these conditions in spite of the rapid allylic rearrangement that such compounds normally undergo. They are readily oxidized to the enantiomeric 2-cyclohexen-1-ols in 93% ee, making these derivatives readily available. Finally, the parent boranes react readily with acetaldehyde and other representative aldehydes to provide the corresponding 1-(2-cyclohexenyl)-1-alkanols in 100% erythro selectivities and 94% ee.

Hoffmann and his co-workers have utilized allylboronic esters prepared from optically active glycols to achieve the asymmetric synthesis of homoallylic alcohols.<sup>1</sup> Unfortunately, the preferred

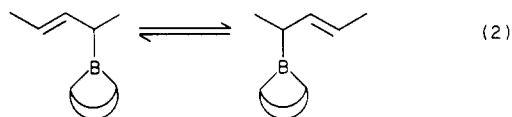
chiral auxiliary must be synthesized by "multistep" procedure. Moreover, the optical purities achieved are usually only in the 60–80% ee range.

We discovered that simple allylic derivatives ( $\text{Ipc}_2\text{BR}$ ;  $\text{R}$  = allyl,<sup>2</sup> 2-methylallyl,<sup>3</sup> 3,3-dimethylallyl;<sup>4</sup>  $\text{Ipc}$  = isopinocampheyl) are readily synthesized and yield the homoallylic alcohols with optical purities in the range of 88–96% ee<sup>5</sup> (eq 1).



There is considerable interest in extending such asymmetric syntheses to the enantioselective synthesis of diastereomers. Indeed, there are several reports describing excellent diastereoselective reactions of allyl metals with aldehydes.<sup>6</sup> However, most of the literature involves use of optically inactive allyl metals. In only two cases have optically active allyl metals been used.<sup>7,8</sup>

The B-crotyl derivatives are known to undergo internal allylic isomerization.<sup>9</sup> The rate of isomerization of these intermediate derivatives varies greatly:  $\text{allyl-BR}_2 > \text{allyl-B(OR')}_2 > \text{allyl-B(OR')}_2$ . Further, the rate of reaction with aldehydes varies in the same order: allyl- $\text{BR}_2$  reacts readily at  $-78^\circ\text{C}$ ,<sup>2</sup> the allyl- $\text{B(OR')}_2$  at  $-15^\circ\text{C} \rightarrow$  room temperature, and the allyl- $\text{B(OR')}_2$  at room temperature.<sup>7</sup> The optical purity achieved is greater the lower the reaction temperature. Thus, the problem in using our approach over the less reactive  $\text{RB(OR')}$  and  $\text{RB(OR')}_2$  was the lack of any knowledge about the practical synthesis of optically active allyldialkylborane ( $\text{R}^*\text{BR}'_2$ ). Such dialkylboranes are known to undergo rapid allylic rearrangement, even at relatively low temperature<sup>9a</sup> (eq 2).



In a symmetrical system, each allylic shift would produce the enantiomer, resulting in a rapid racemization. Accordingly, the first hurdle in examining the feasibility of extending our allylboration to the synthesis of optically active diastereomers involved testing the possibility of synthesizing an optically active chiral allylborane,  $\text{R}^*\text{BIpc}_2$ , to see if such compounds could retain their optical activity sufficiently long to be useful for asymmetric synthesis.

1,3-Cyclohexadiene was treated with  $\text{Ipc}_2\text{BH}$  [from (+)- $\alpha$ -pinene] at  $-25^\circ\text{C}$ . The reaction product was oxidized at  $0^\circ\text{C}$  with trimethylamine N-oxide.<sup>10</sup> There was obtained a 92:8 mixture of (S)-(-)-2-cyclohexen-1-ol,  $[\alpha]_D^{25} -104.5^\circ$  (c 1.0,  $\text{CHCl}_3$ ), 93% ee,<sup>11</sup> and 3-cyclohexen-1-ol (eq 3).

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