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# Dimerization of Cyclopropparenes by Silver Ion

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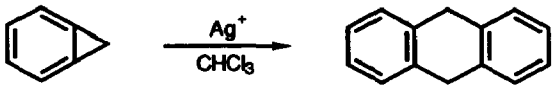
**Keywords:** Cyclopropparenes; acene; biscyclopropparene; polyacene.

**Abstract:** Cyclopropparenes react with silver ion in chloroform to yield dimers which can be aromatized by dichlorodicyanoquinone in benzene to give the corresponding acene.

The manufacture and manipulation of structures at a molecular level has been recognized as an important goal for more than thirty years.[1] The synthesis of linear rigid molecules composed primarily of six-membered rings (molecular lines) is of interest in this regard. Miller and his co-workers have prepared short molecular lines composed of polyacenequinone units via repetitive Diels-Alder reactions.[2,3] The Diels-Alder reaction has also been identified as a route to novel belts or collars.[4-6] We present here a convenient route to six-membered rings using cyclopropparenes[7] as starting materials.

The reaction is exemplified below using the simplest cyclopropparene, benzocyclopropene. Other examples are presented in Table I.




1 2

In a typical experiment a solution of the cyclopropparene (200-500 mg) in about 15 mL of anhydrous chloroform was added dropwise to a stirred suspension of $AgBF_4$ (≈ 1 mole %) in 25 mL of anhydrous chloroform at 0 °C under argon. The reaction was usually complete after 10 min. The catalyst could be removed by filtration through florisil.

These facile reactions probably arise via cationic intermediates resulting from addition of the silver ion to the sigma electrons of the cyclopropenyl ring.[8-17] A possible mechanism is presented in Scheme 1.

**Scheme 1**

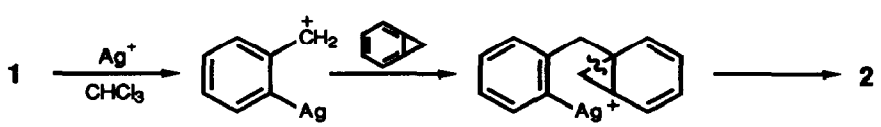
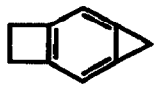
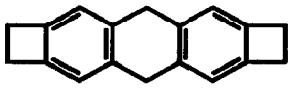
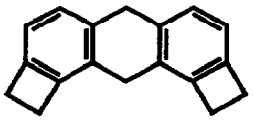
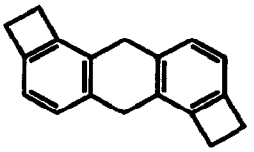
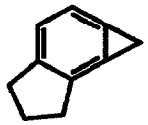
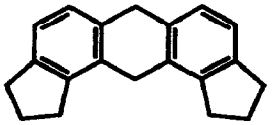
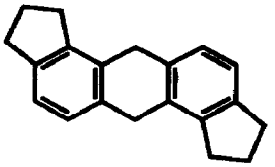
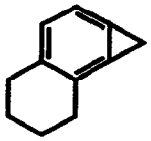
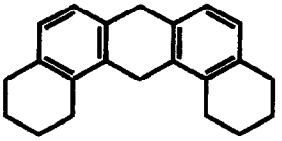
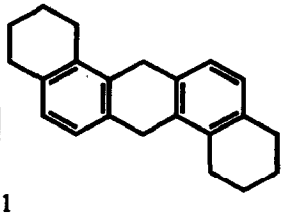
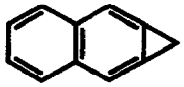
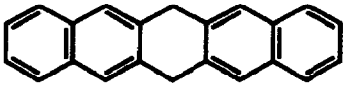
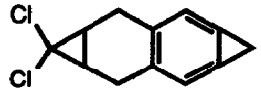
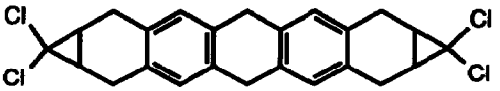


**Table I. Dimerization of Cycloproparenes by Silver Ion**

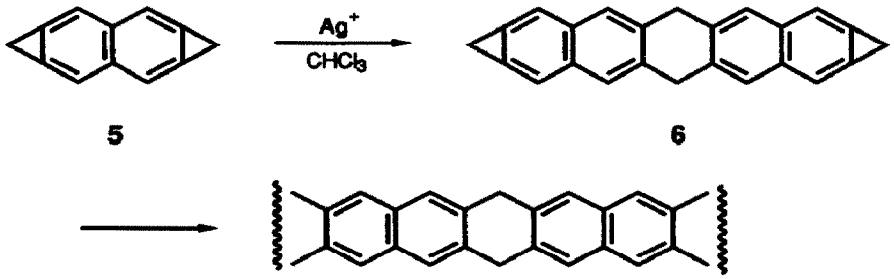
| Cycloproparene | Product(s) Ratio | Yield[a] % |
|---|---|---|
|  |  | 95 |
|  |   61:39 | 70 |
|  |   59:41 | 78 |
|  |   19:81 | 80 |
|  |  | 83 |
|  |  | 95 |

[a] Yields are based on isolated products and are combined yields for those reactions which yield two products.

Aromatization of the dimers presented in Table I provides a convenient synthesis of the corresponding acenes. For example, treatment of **3** with DDQ in benzene for 1 hour yields anthracene **4** in 87% yield.


**3** **4**

The prospect that the polyacenes, or highly conjugated ladder polymers,[18] might exhibit interesting properties including high temperature superconductivity[19] has led to a flurry of activity in this area.[18, 20-26] Simple iterative chain-growing reactions using biscycloproparenes[27, 28] should lead to materials which upon aromatization would yield these polyacenes. We have investigated the oligomerization of **5** using silver ion




**5** **6**

and we find that polymerization does occur. The reaction can be monitored by NMR in $CDCl_3$ and the initial product formed is **6**. ($^1$H NMR (300 MHz) δ 7.83 (4H), 7.54 (4H), 4.23 (4H), 3.50 (4H)). As the chain length increases the oligomers precipitate from solution. Characterization of the resulting thermally stable materials is currently underway.

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## References and Notes

1. The publication of Feynman [*Saturday Review* **1960**, *46*, 45] seems to have inspired much of the interest in this field of research.
2. Kenny, P. W.; Miller, L. L. *J. Chem. Soc. Chem. Commun.* **1988**, 84.
3. Kenny, P. W.; Miller, L. L.; Rak, S. F.; Jozefiak, T. H.; Christopfel, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 4445.
4. Kohnke, F. H.; Stoddart, J. F. *Pure and Appl. Chem.* **1989**, *61*, 1581.

5. Kohnke, F. H.; Mathias, J. P. Stoddart, J. F. *Angew. Chem. Int. Ed. Engl. Adv. Mater.* **1989**, *28*, 1103.
6. Mathias, J. P.; Stoddart, J. F. *Chem. Soc. Revs.* **1992**, *21*, 215.
7. Billups, W. E.; Rodin, W. A.; Haley, M. M. *Tetrahedron* **1988**, *44*, 1305. Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349; *Chem. Rev.* **1989**, *89*, 1161.
8. Billups, W. E.; Rodin, W. A. *J. Org. Chem.* **1988**, *53*, 1312.
9. Bee, L. K.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7076.
10. Paquette, L. A.; Wilson, S. E.; Henzel, R. P. *J. Am. Chem. Soc.* **1972**, *94*, 7771.
11. Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7748.
12. Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 4597.
13. Sakai, M.; Masamune, S. *J. Am. Chem. Soc.* **1971**, *93*, 4610. Sakai, M.; Westberg, H. H.; Yamaguchi, H.; Masamune, S. *J. Am. Chem. Soc.* **1971**, *93*, 4611.
14. Paquette, L. A.; Allen, G. R., Jr.; Henzel, R. P. *J. Am. Chem. Soc.* **1970**, *92*, 7002.
15. Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6366.
16. Danben, W. G.; Schallhorn, C. H.; Whalen, D. L. *J. Am. Chem. Soc.* **1971**, *93*, 1446.
17. For reviews and further references, see *Advanced Organic Chemistry 3rd ed.*, March, J.; John Wiley and Sons, Inc: New York, 1985; pp. 1039-1041. *Advanced Organic Chemistry Part B: Reactions and Synthesis*, Carey, F. A.; Sundberg, R. J.; Plenum Press: New York, 1977; pp. 191-193. Paquette, L. A. *Synthesis* **1975**, pp. 347-357. Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, pp. 280-287; Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461-486. Cardin, D. J.; Cetinkaya, B.; Doyle, M. J.; Lappert, M. F. *Chem. Soc. Rev.* **1973**, *2*, 99-144 pp. 132-139.
18. Bailey, W. J. *Encyclopedia of Polymer Science and Engineering 2nd ed.*, Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges; G.; Kroschwitz, J. I. Eds.; John Wiley and Sons, Inc: New York, 1990; pp. 158-235.
19. Kivelson, S.; Chapman, O. L. *Phys. Rev. B.* **1983**, *28*, 7236.
20. Tanaka, K.; Ohzeki, K.; Yamabe, T.; Yata, S. *Synthetic Metals* **1984**, *9*, 41.
21. Mishima, A.; Kimura, K. *Synthetic Metals* **1985**, *11*, 75; Aono, S.; Nishikawa, K.; Kimura, M.; Kawabe, H. *Synthetic Metals* **1987**, *17*, 167.
22. Ozaki, M.; Ikeda, Y.; Nagoya, I. *Synthetic Metals* **1989**, *28*, C801. Ozaki, M.; Ikeda, Y.; Nagoya, I. *Synthetic Metals* **1987**, *18*, 485.
23. Marvel, C. S.; Levesque, C. L. *J. Am Chem. Soc.* **1938**, *60*, 280.
24. Bailey, W. J.; Fetter, E. J.; Economy, J. *J. Org. Chem.* **1962**, *27*, 3479.
25. Kiji, J.; Iwamoto, M. *J. Polym. Sci. Polym. Lett. Ed.* **1968**, *6*, 53.
26. Patent: Jpn. Kokai Tokkyo Koho 62 179, 509 (Aug. 6, 1987), Kitamura, T.; Hasumi, K.; and Fujisawa, N. (to Dainippon Ink and Chemicals, Inc.)
27. Ippen, J.; Vogel, E. *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 736.
28. Billups, W. E.; Haley, M. M.; Claussen, R. C.; Rodin, W. A. *J. Am. Chem. Soc.* **1991**, *113*, 4331.


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