

1,2-DIBROMOPYRACYLENE: A NEW AROMATIC SYSTEM

Barry M. Trost and David R. Brittelli

Department of Chemistry, University of Wisconsin

Madison, Wisconsin 53706

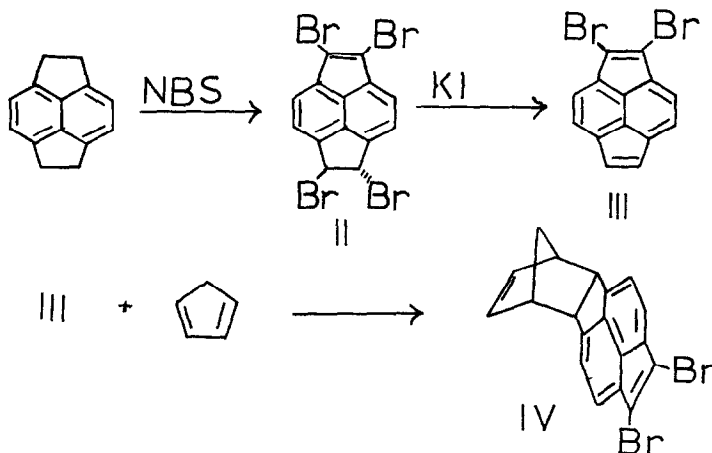
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Pyracylene is a $4n+2$ aromatic hydrocarbon that is predicted to possess an empty non-bonding molecular orbital.¹ In our previous studies,² we prepared a derivative of this system, pyracyloquinone, which we have been unable to reduce to the desired aromatic. Our studies of this quinone and the radical anion derived from it led us to believe that pyracylene did not possess the substantial delocalization energy predicted by molecular orbital theory. We wish now to report the synthesis of the first member of this family of aromatics, 1,2-dibromopyracylene, which is remarkably stable but highly reactive.

During our studies to find the best method for conversion of acenaphthenes to acenaphthylenes, we found that treatment of acenaphthene with excess N-bromosuccinimide

(NBS) produced over 90% yields of 1,2-dibromoacenaphthylene. Therefore, we attempted to apply this reaction to the synthesis of 1,2,5,6-tetrabromopyracylene I by bromination of pyracene. Even with large excesses of NBS and long reaction times, none of I could be detected in the crude reaction mixtures. However, two products were isolated. The major one, m.p. 195-196°, showed an AB pattern for 4H with H_A at 7.78 p.p.m., H_B at 7.60 p.p.m. and $J_{AB} = 7.0$ c.p.s. and a singlet for 2H at 5.94 p.p.m. The ultraviolet spectrum showed maxima ($\log \epsilon$) at 368 mu (3.95), 352 mu (4.09), 335 mu (4.16) and 225 mu (4.78)-typical of dibromo-acenaphthylenes.³ Combined with mass spectral data⁴ and elemental analysis⁵ which establish the formula as $C_{14}H_6Br_4$, structure II (see Scheme I) must be assigned.

Scheme I. Preparation of 1,2-Dibromopyracylene



Compound II smoothly eliminated the elements of bromine upon treatment with powdered potassium iodide in refluxing acetone to produce the first member of the pyracylene family, 1,2-dibromopyracylene, m.p. 95 dec.⁵ The ultraviolet spectrum shows maxima ($\log \epsilon$) at 391 mu (3.16), 363 mu (4.14), 355 mu (3.92), 346 mu (4.18), 339 mu (3.96), 331 mu (4.01), 317 mu (3.76), 303 mu (3.51), 261 mu (3.88), and 222 mu (4.73). Its n.m.r. spectrum showed an AB pattern for 4H with H_A at 6.85 p.p.m., H_B at 6.69 p.p.m. and $J_{AB} = 7.0$ c.p.s. and a 2H singlet at 6.28 p.p.m.⁶

The Diels-Alder reaction of III provided further supporting evidence. Condensation of 1,2-dibromopyracylene with cyclopentadiene proceeds at 25° in almost quantitative yield to form the 1:1 adduct IV.⁵ The adduct had ultraviolet absorption ($\log \epsilon$) at 377 mu (3.99), 369 mu (3.95), 359 mu (4.10), 343 mu (3.97), 328 mu (4.09), 314 mu (3.75), 300 mu (3.38) and 245 mu (4.42). Its n.m.r. shows an AB pattern for 4H with H_A at 7.52 p.p.m., H_B at 7.28 p.p.m. and $J_{AB} = 7.0$ c.p.s., (aromatic ring protons) a 2H triplet at 5.32 p.p.m. with $J = 2.0$ c.p.s. (olefinic protons), a 2H doublet at 4.20 p.p.m. with $J = 3.0$ c.p.s. (benzylic protons), a 2H multiplet at 3.22 p.p.m. (bridgehead protons), and a 2H triplet at 1.90 p.p.m. with $J = 1.5$ c.p.s. (methylene bridge protons). The 3 c.p.s. coupling of the benzylic protons with the bridgehead protons indicates the endo configuration

as depicted.⁷ The absorptions of the norbornene ring in the n.m.r. are very similar to the corresponding absorptions in the spectrum of the benzoquinone-cyclopentadiene adduct.

Thus, contrary to our expectations based on our previous studies,² the pyraclyene system does possess the stability predicted by molecular orbital theory. The extreme ease with which 1,2-dibromopyraclyene undergoes the Diels-Alder reaction does not demonstrate lack of aromaticity. If the initial step in the Diels-Alder reaction involves a charge-transfer complex,⁸ the fact that the pyraclyene system should be an extremely good pi acid might lead one to expect a facile Diels-Alder reaction with dienes.

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References

1. R. D. Brown, J. Chem. Soc., 2391 (1951).
2. a) B. M. Trost, J. Am. Chem. Soc., 88, 853 (1966);
b) B. M. Trost and S. F. Nelsen, ibid., 88, 2876 (1966).
3. B. M. Trost and D. R. Brittelli, unpublished observations.
4. We wish to thank Professor L. A. Singer for this determination.
5. Satisfactory elemental analyses were obtained for all new compounds.
6. The unusual n.m.r. spectrum will be discussed in more detail in the full paper.
7. P. M. Subramanian, M. T. Emerson, and N. A. LeBel, J. Org. Chem., 30, 2625 (1965).
8. R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," S. Patai, ed., Interscience Publishing Co., New York, N.Y., 1964, pp. 878-929.