Tetrahedron Letters No. 22, pp 1893 - 1896, 1978. 0040-4039/78/0522-1893$02.00/0
©Pergamon Press Ltd. Printed in Great Britain.

STRAINED POLYCYCLIC AROMATIC MOLECULES - I

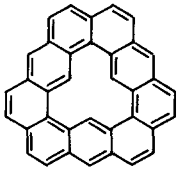
SYNTHESIS OF 9-BROMODINAPHTH[1,2-a:2',1'-j]ANTHRACENE

C.F. Wilcox, Jr., P.M. Lahti, J.R. Rocca, M.B. Halpern and J. Meinwald

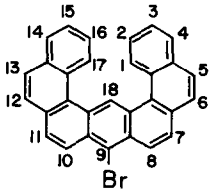
Department of Chemistry, Cornell University, Ithaca, New York 14853

(Received in USA 27 February 1978; received in UK for publication 3 April 1978)

Our interest in aromatic molecules related to [9]-coronaphene, I (1-5), has prompted us to prepare 9-bromodinaphth[1,2-a:2',1'-j]anthracene, II, a more accessible molecule that nevertheless has a carbon framework and three crowded, "internal" hydrogen atoms similar to those in I. The strain energy of II, which results from these three crowded hydrogens and the distorted carbon framework necessary to accommodate them, would appear from molecular models to be large. The strain energy of I should be even greater than that of II because of its closed perimeter of six-membered rings. We prepared II by a photocyclization that has proven effective in the preparation of many helicenes and related strained molecules (6-11).



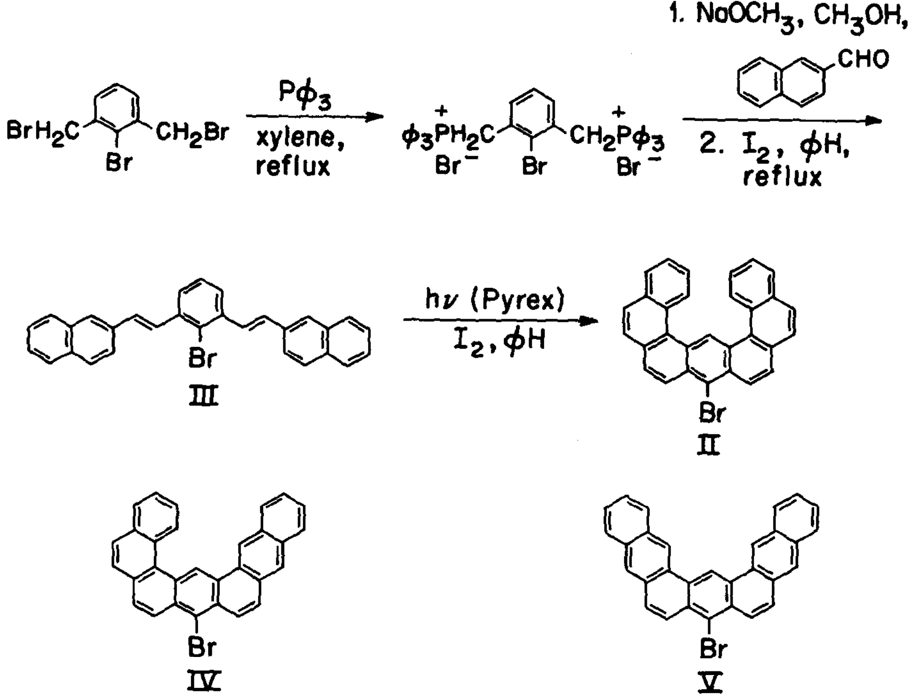
I



II

The synthetic route to II is outlined in Chart I. α,α',2-Tribromo-m-xylene was prepared by the method of Vögtle (12). Reaction of this compound with 2.0 mol-equiv. of triphenylphosphine in refluxing xylene followed by crystallization (CH_2Cl_2/THF) gave an 85% yield of 2-bromo-α,α'-bis(triphenylphosphonio)-m-xylene dibromide, mp>260°C d. A bromine atom was incorporated into the key intermediate, 2-bromo-1,3-bis[2-(2-naphthyl)vinyl]benzene, III, to prevent cyclization from occurring at C(2) (6). To simplify its purification and characterization, III was converted to

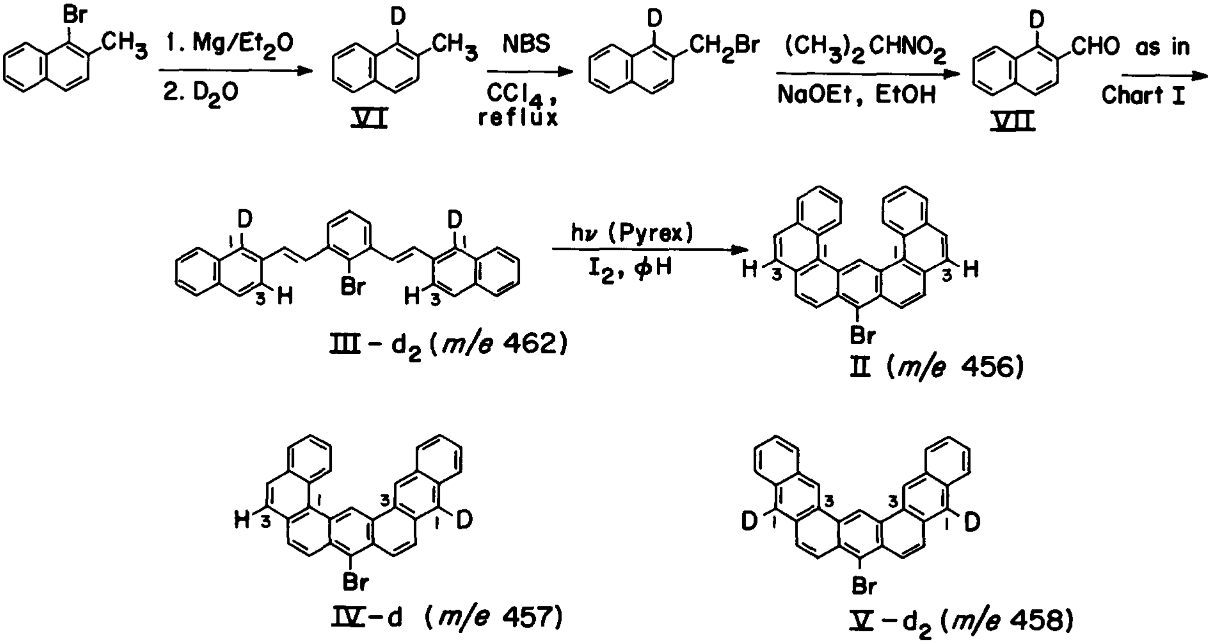
Chart I



the trans, trans isomer, mp 222-4°C by refluxing the crude Wittig reaction product with iodine in benzene. In principle, photocyclization-dehydrogenation of III might give any of three structures (II, IV, or V), but there were grounds for hoping that cyclizations at the 1-positions of both naphthalene rings would be favored, giving the desired ring system (7). Irradiation of 100 mg of III in 1 liter of benzene containing 10 mg of iodine (Hanovia 450 watt medium pressure mercury lamp through Pyrex for 3 hr), followed by crystallization of the crude photo-product from benzene/methanol, gave 62 mg of II as tiny, yellow, non-fluorescent needles, mp 305-8°C. In a different work-up of this reaction, the crude product was chromatographed (neutral alumina/hexane, ethyl acetate) and crystallized (CS_2/ethyl acetate) giving 33 mg of II (from 150 mg of III) showing mp 312-4°C. The high resolution mass spectrum of the product contained a molecular ion consistent with its formulation as $C_{30}H_{17}Br$ (calcd. m/e: 456.0511, 458.0491; obsvd. m/e: 456.0503, 458.0502). It had the following absorptions in its ultraviolet spectrum ($\lambda_{max}^{CH_2Cl_2}$, log ϵ): 289 nm, 4.48; 338 nm, 4.89; 393 nm, 3.88. The most compelling evidence for the assignment of structure II to this compound was the presence of a one-proton singlet at δ 10.85 ppm in its ^1H nmr spectrum. Only structure II appears to contain a proton, the unique one at C(18), which would resonate at such low field (*cf*. ref. 5). The remainder of the ^{1}H nmr spectrum of II showed the following resonances (90 MHz, CS$_2$ soln.): δ 8.82, d, J = 8 Hz, 2H at C(1,17); δ 8.57, d, J = 9 Hz, 2H at C(8,10); δ 8.15-7.70, m, 8H at C(4-7,11-14); δ 7.65-7.25, m, 4H at C(3,4,15,16).

Because the arguments favoring structure II presented so far are suggestive rather than definitive, and because of the unusual geometry at the center of the desired molecule, we carried out a labeling experiment similar to those used by Martin *et al*. (8,9), which discriminates unambiguously among the possible cyclized products. The synthesis of 2-bromo-1,3-bis[2-(2-naphthyl-*1-d*)vinyl]benzene, III-d$_2$, and the logic behind this experiment are outlined in Chart II. 2-Bromomethylnaphthalene-*1-d* was oxidized to VII using the method of Hass and Bender (13). The ^{1}H nmr and mass spectra of VI and the ^{1}H nmr spectrum of VII indicate that these intermediates were approximately 85% deuterated (14). This, along with the mass spectrum of III-d$_2$, suggests that our bis-(naphthylvinyl)benzene was approximately 70% doubly deuterated. Photocyclization-dehydrogenation of III-d$_2$ gave a deuterium-free product, as required for II. Thus, we conclude that II was formed in spite of the extensive crowding of the three central hydrogens. These results rule out IV-d (loss of 3H and 1D) and V-d$_2$ (loss of 4H) as the major photo-product. No effort was made to characterize any minor reaction products.

Chart II



Although the utility of photocyclization-dehydrogenation in the synthesis of a coronaphene is yet to be shown, our results suggest that this method may well have promise for the preparation of [9]-coronaphene .

Acknowledgements: We are indebted to the National Science Foundation (Grant No. CHE 76-82122 A 01) for partial support of this research, and to the NSF-Undergraduate Research Participation program for financial assistance given to P.M.L. and M.B.H. during the summer of 1977. We would also like to acknowledge the assistance given to us by T. Wachs and J. Shea of the Cornell Mass Spectrometry Facility.

REFERENCES

(1) W. Jenny and R. Peter, *Angew. Chem. Internat. Edit.*, **4**, 979 (1965).
(2) R. Peter and W. Jenny, *Helv. Chim. Acta*, **49**, 2123 (1966).
(3) K. Burri and W. Jenny, *Helv. Chim. Acta*, **50**, 2542 (1967).
(4) W. Jenny and R. Paioni, *Chimia*, **23**, 41 (1969).
(5) F. Vögtle and H.A. Staab, *Chem. Ber.*, **101**, 2709 (1968).
(6) R.H. Martin, Ch. Eyndels, and N. Defay, *Tetrahedron Letters*, 2731 (1972).
(7) W.H. Laarhoven, Th. J. H. M. Cuppen, and R.J.F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **87**, 687 (1968); *Tetrahedron*, **26**, 1069, 4865 (1970).
(8) R.H. Martin and J.J. Schurter, *Tetrahedron Letters*, 3679 (1969).
(9) R.H. Martin, G. Morren, and J.J. Schurter, *Tetrahedron Letters*, 3683 (1969).
(10) R.H. Martin, M.J. Marchant, and M. Baes, *Helv. Chim. Acta*, **54**, 358 (1971).
(11) R.H. Martin and M. Baes, *Tetrahedron*, **31**, 2135 (1975).
(12) F. Vögtle, *Chem. Ber.*, **102**, 1788 (1969).
(13) H.B. Hass and M.L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).
(14) A superior method for accomplishing the bromine-deuterium exchange of which we became aware only after carrying out the experiments reported here involves refluxing the brominated compound with Zn and CaO in D_2O for 48 hours. This method gave VI with greater than 95% deuterium incorporation from 1-bromo-2-methylnaphthalene (*cf.* ref. 8 and also B. Chenon, L.C. Leitch, R.N. Renaud and L. Pichat, *Bull. Soc. Chim. France*, 38 (1964).