Tetrahedron Letters,Vol.27,No.20,pp 2231-2234,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

DIRECTIVE EFFECT OF BROMINE ON STILBENE PHOTOCYCLIZATIONS. AN IMPROVED SYNTHESIS OF [7]HELICENE[#]

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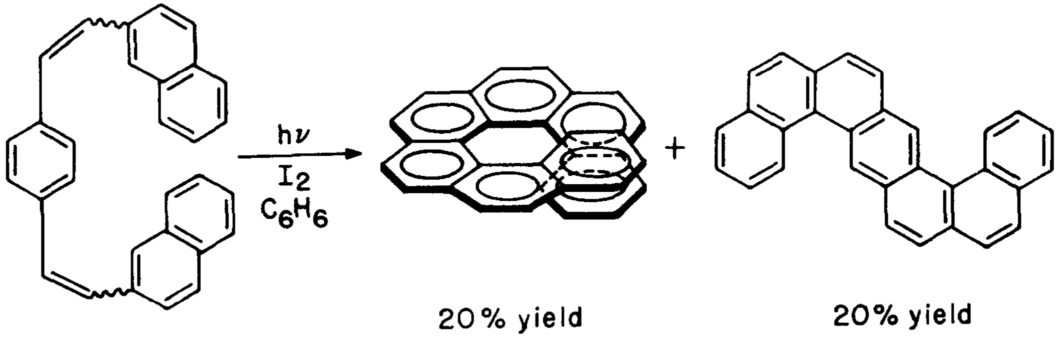
Summary: Bromine atoms direct photocyclizations away both from positions they occupy and from those adjacent, providing previously unavailable selectivities in syntheses of [7]helicenes.

Stilbene photocyclizations would be more useful in synthesis if, when reactions choose between alternative courses, procedures were available to steer them in the directions desired.[1] For example, although the procedure in eq 1 gives [7]helicene (**2**), it also gives an equal amount of **3** by following an alternate direction of cyclization.[2]



(1)

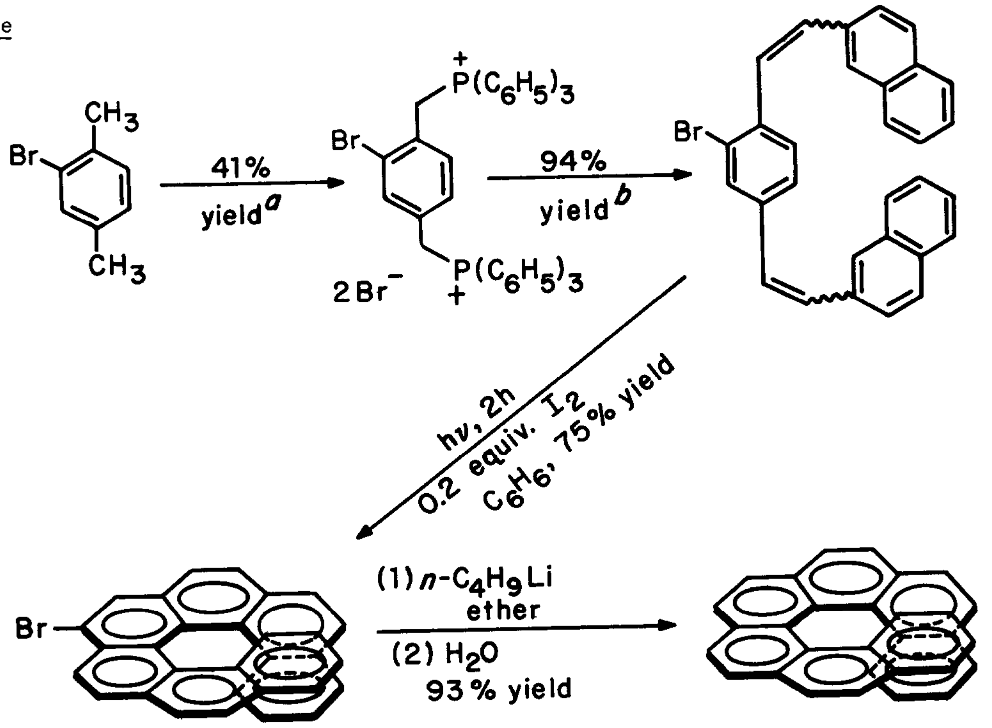
1 **2** **3**

We have discovered that a bromine atom appended to the benzene ring of **1** can direct the photocyclization to give the helical product contaminated with less than 10% of its planar isomer (see the Scheme). Moreover, as the bromine is both easily incorporated and removed, this procedure is the simplest available for synthesizing [7]helicene.

Although Martin et al.[3] and Wilcox et al.[4] had previously introduced bromine atoms into molecules to direct photocyclizations, Mallory et al. recently pointed out that those examples provide no evidence for a directive effect;[5a] removing the bromine atoms does not redirect the reactions.[5]

[#] Dedicated to Professor Harry H. Wasserman on his sixty-fifth birthday.

Scheme



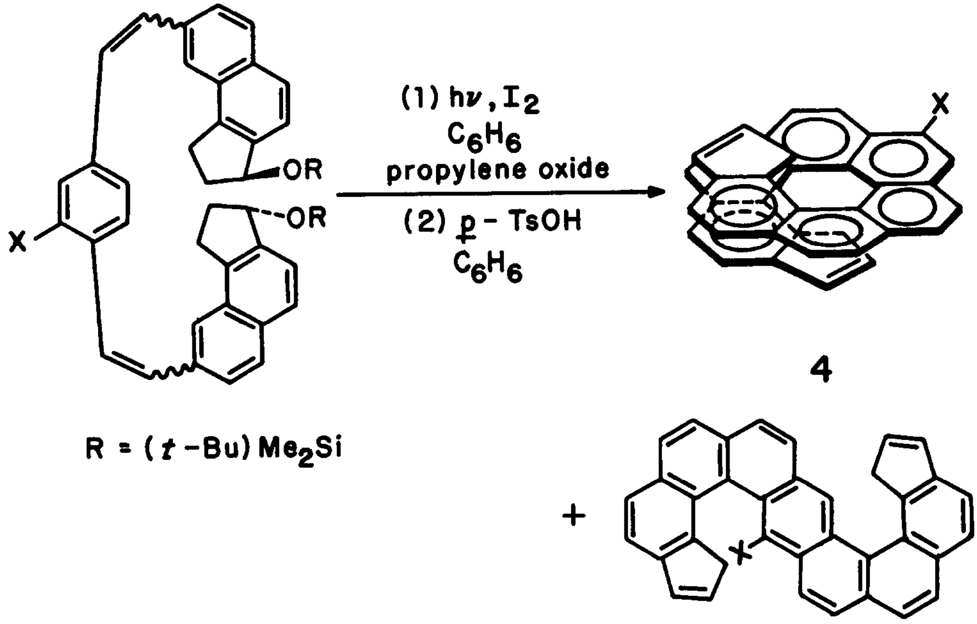
2

[a] N-bromosuccinimide (2.2 equiv) + $(C_6H_5CO_2)_2$ (0.008 equiv) in refluxing CCl_4 (3 h), >46% yield; then $(C_6H_5)_3P$ in refluxing $(CH_3)_2NCHO$ (3 h), 91% yield. [b] 2-naphthaldehyde (2 equiv) + $LiOC_2H_5$ (6 equiv) in C_2H_5OH (17 h).

In the Scheme and in a related transformation below the bromine does have the effect previously sought. Furthermore, it guides the cyclizations away not only from the position occupied, for which precedents are numerous,[1a,6,7] but also from the position adjacent, for which there is only a single precedent, one that does not involve a choice between different carbon skeletons.[8]

The effect of bromine in the photocyclization in the Scheme is significant because it allows accessible materials to be used for the synthesis. Although alternative preparations of [7]helicene[1c,7a] do not require bromine to achieve selectivity, they do require precursors that, compared to 2-bromo-p-xylene and 2-naphthaldehyde, are more difficult to synthesize in quantity.[9] In the case of related syntheses that incorporate additional substituents, the bromine's effect can be crucial.

Consider, for example, how the difficulties associated with the synthesis of [7]helicene are magnified when attempts are made to synthesize the substituted derivative 4.[10] The approaches involving photocyclizations of bis(3-phenanthrenyl)ethenes require precursors, such as 1-*H*-cyclopenta[c]phenanthrene-10-carboxaldehyde, for whose synthesis in quantity no easily adaptable procedures seem available.[11] And for this approach, as well as the alternative outlined in eq 2, the hindering saturated substituents on the aromatic rings should diminish the yield of helical product to even less than the 20% achieved in eq 1.



R = (*t*-Bu)Me$_2$Si

4

(2)

5

Indeed when X = H, the photocyclization in eq 2 gives a 65% yield of **5**, the analogue of **3**, and no detectable material with the skeletal structure of 4.[12] We describe elsewhere how this hydrocarbon can be prepared in 80% yield, uncontaminated by **5**, by employing a bromine substituent to direct the photocyclization.[13] However, the point we make here is that, in contrast to the report of Mallory mentioned above,[5] removing the bromine does redirect the reaction.

Acknowledgement. We are grateful for the support of the National Science Foundation (DMR-82-13794) and the National Institutes of Health (RO1-GM-34737).

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(7) Cyclizations in the following references are also probably directed by bromine, although the paths followed when it is absent are unexplored. (a) M. Gorsane, N. Defay, and R. H. Martin, *Bull. Soc. Chim. Belg.*, **94**, 215 (1985). (b) F. B. Mallory and C. W. Mallory in reference 1a, p. 173. (c) M. Joly, N. Defay, and R. H. Martin, *Helv. Chim. Acta*, **60**, 537 (1977).

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(9) For example, 3-methylphenanthrene: (a) B. F. Bonini and M. Tiecco, *Gazz. Chim. Ital.* **96**, 1792 (1966); (b) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964); (c) R. D. Haworth, *J. Chem. Soc.* **1932**, 1125; (d) R. Pschorr, *Chem. Ber.* **39**, 3106 (1906).

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(11) Sudhakar[10] in Chapter 5 examines syntheses of such precursors. In sum, the hurdles that seemingly have to be surmounted include these: the small scale required when photocyclizations are used to prepare precursor phenanthrenes that themselves must be carried through many steps; poor directional selectivities in the Friedel-Crafts cyclization of 3-(6-bromophenanthrenyl)propanoic acid and in the photocyclizations of 5-(2-phenylethenyl)-2,3-dihydro-1*H*-indenes; and the reactivity of phenanthrene's 9- and 10-positions.

(12) The ^{1}H NMR spectrum of the crude product exhibits no resonances characteristic of **4**, but accords with structure **5**, the position of a peak at $\delta 8.96$ (s, 1.92H) being notable [R. H. Martin, *Tetrahedron*, 897 (1964); R. H. Martin, N. Defay, F. Greets-Evard, and S. Delavarenne, *Ibid.*, 1073 (1964)].

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(Received in USA 22 January 1986)