Tetrahedron Letters Vol, 21, pp 217 - 220
©Pergamon Press Ltd. 1980. Printed in Great Britain.

0040-4039/80/0108-0217$02.00/0

5,12-DIHYDRO-6,11-DIDEHYDRONAPHTHACENE, A DERIVATIVE OF 1,4-DIDEHYDRONAPHTHALENE[+]

Henry N.C. Wong* and Franz Sondheimer*
Chemistry Department, University College London,
20 Gordon Street, London WC1H OAJ, England.

Summary Treatment of the di-lithium derivative of 1,2-diethynylbenzene (1) with o-xylene-α,α'-diol di-p-toluenesulphonate (2) in tetrahydrofuran led to 5,12-dihydronapthacene (5) as the only identifiable product. This reaction presumably involves 5,12-dihydro-6,11-didehydronapthacene (4) as an intermediate, and this was confirmed by the formation of 5,12-dihydro-6,11-dideuterionaphthacene when the reaction was carried out in tetrahydrofuran-d_8.

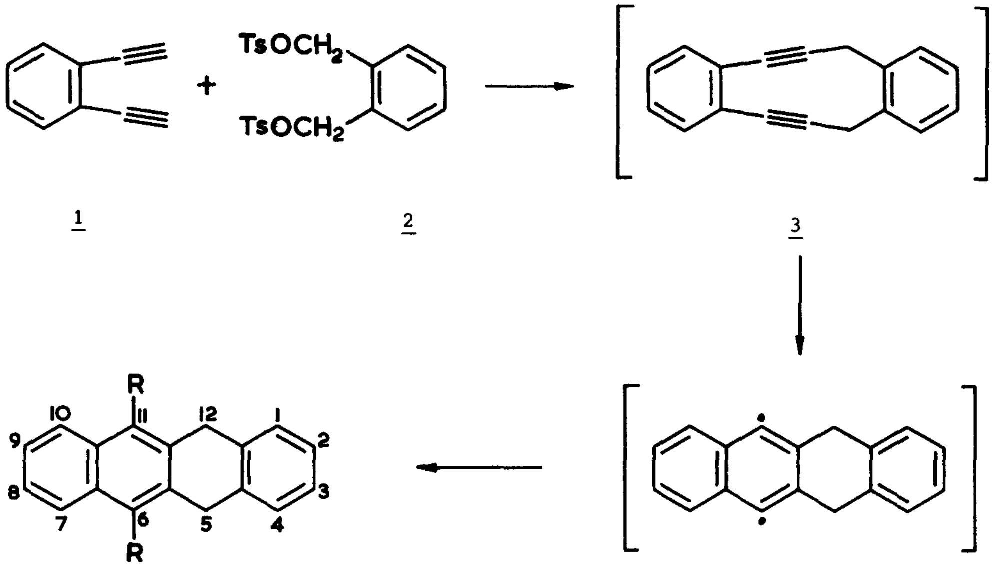
Although 1,8-didehydronaphthalene has been obtained as an intermediate several years ago,[1] no other didehydronaphthalene has been claimed. We now report a reaction, which most probably involves the 1,4-didehydronaphthalene derivative (4) (5,12-dihydro-6,11-didehydronaphthacene) as an intermediate.

In an attempt to prepare the dibenzannelated cyclodeca-1,5-diyne (3), the dilithium derivative of 1,2-diethynylbenzene (1)[2-4] [prepared from (1) and n-butyllithium (2 molar equiv.) in tetrahydrofuran at -10°] was allowed to react with an equimolar amount of o-xylene-α,α'-diol di-p-toluenesulphonate (2)[5] (m.p. 89-90°) in tetrahydrofuran at -10° and then at room temperature. The only identifiable product, isolated in 4% yield by chromatography on silica gel, proved to be 5,12-dihydronaphthacene (5)[7],

---

[+] This contribution is dedicated with respect and affection to the memory of the late Professor R.B. Woodward.

colourless needles, m.p. 210-212° m/e 230 (M^+, 100%), 228 (M^+ -2H, 71%); ^{1}H-NMR, ($CDCl_3$, 60MHz) τ 2.10-2.45 (m, 4H, with a singlet at 2.28), 2.45-2.90 (m, 6H), 5.92 (s, 4H).



1 2 3

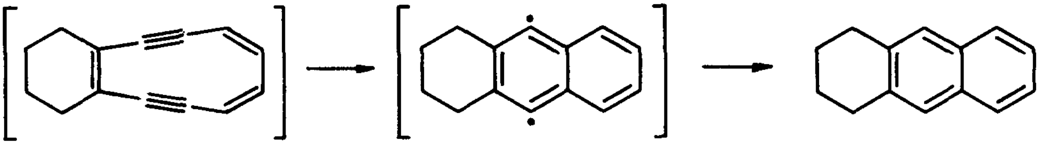
4

5, R = H

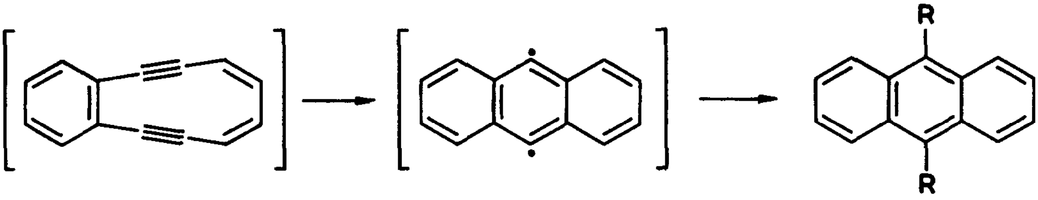
6, R = D

Compound (5) was most probably formed from (1) and (2) by formation of dibenzocyclodeca-1,6-diene-4,8-diyne (3), followed by ring closure to 5,12-dihydro-6,11-didehydronaphthacene (4) and subsequent addition of protons. This was confirmed by the results obtained when the above described reaction was carried out in tetrahydrofuran-d_8, whereby the 6,11-dideurio compound (6) was obtained. The structure of this substance was established by the mass spectrum [m/e 232 (M^+, 100%) 230 (M^+ - 2H, 91%)] and the ^{1}H-NMR spectrum ($CDCl_3$,60MHz), in which the 2H singlet at τ2.28 assigned to H-6 and H-11 in (5) had disappeared.

The above described results bear some similarity to the formation of 1,2,3,4-tetrahydroanthracene (9) from a reaction which should have led to the cyclohexeneannelated 1,5-bisdehydro[10]annulene (7)[8]. This reaction presumably proceeds via the 1,4-didehydronaphthalene derivative (8), although this possibility was not discussed [the additional formation of benzocyclodec-3-ene-1,5-diyne in this reaction[8] may also



7 8 9



10 11 12, R = H

13, R = D

involve the 1,4-didehydronaphthalene (8) as an intermediate]. Confirmation of this mechanism is provided by the exclusive formation of anthracene (12) [or 9,10-dideuterioanthracene (13)] from a reaction[8] which should have led to the benzannelated 1,5-bisdehydro[10]annulene (10), by a path presumably proceeding via 9,10-didehydroanthracene (11).[9]

The above described formation of 1,4-didehydronaphthalenes from *cis*-hex-3-ene-1,5-diyne derivatives paralles the generation of 1,4-didehydrobenzene ("*p*-benzyne") from *cis*-hex-3-ene-1,5-diyne itself,[10] although this reaction has been carried out in the gas phase.[11]

Acknowledgement

One of us (H.N.C.W.) thanks the Ramsay Memorial Fellowships Trust for a British (General) Fellowship.

References and Notes

1. C.W. Rees and R.C. Storr, *J.C.S.Chem.Comm.*, 193 (1965).
2. 1,2-Diethynylbenzene (**1**)[3,4] was most readily prepared by treatment of *o*-bis(α,β-dibromoethyl)benzene[3] with excess potassium *t*-butoxide in tetrahydrofuran at room temperature for 2 hours.
3. R.Deluchat, *Compt.rend.*, **192**, 1387 (1931).
4. O.M. Behr, G. Eglinton, A.R. Galbraith, and R.A. Raphael, *J.Chem.Soc.*, 3614 (1960).
5. Prepared in 13.5% yield from *o*-xylene-α,α'-diol by successive treatment with sodium hydride (2 molar equiv.) in boiling ether, and then with *p*-toluenesulphonyl chloride (2 molar equiv.) in ether at -10°.[6]
6. Method of J.K.Kochi and G.S. Hammond, *J.Am.Chem.Soc.*, **75**, 3443 (1953).
7. S. Gabriel and E. Leupold, *Ber.*, **31**, 1272 (1898); J.W. Larsen and L.W. Chang, *J.Org.Chem.*, **44**, 1168 (1979).
8. N. Darby, C.U. Kim, J.A. Salaün, K.W. Shelton, S. Takada, and S. Masamune, *J.C.S.Chem.Comm.*, 1516 (1971).
9. O.L. Chapman, C.-C. Chang, and J. Kolc, *J.Am.Chem.Soc.*, **98**, 5703 (1976). These authors had already discussed the possible intermediacy of (**11**) in the conversion of (**10**) to (**12**).[8]
10. R.R. Jones and R.G.Bergman, *J.Am.Chem.Soc.*, **94**, 660 (1972).
11. It is also of interest to note that Deluchat[3] has reported the formation of naphthalene by dehydrobromination of *o*-bis(α,β-dibromoethyl)benzene with potassium hydroxide in ethanol. This reaction seems to implicate 1,4-didehydronaphthalene itself as an intermediate, but unfortunately we have not been able to duplicate this result.

(Received in UK 30 October 1979)