Tetrahedron Letters No. 30, pp 3067 - 3070, 1972. Pergamon Press. Printed in Great Britain.

THERMAL REACTIONS OF 1,4-BRIDGED-1,2,3,4-TETRAHYDRONAPHTHALENE DERIVATIVES

H.Heaney, S.V.Ley, A.P.Price, and R.P.Sharma

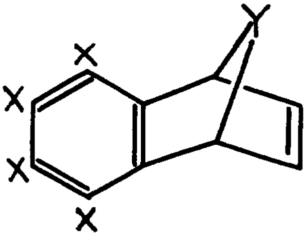
Department of Chemistry, The University of Technology, Loughborough,

Leicestershire, LE11 3TU

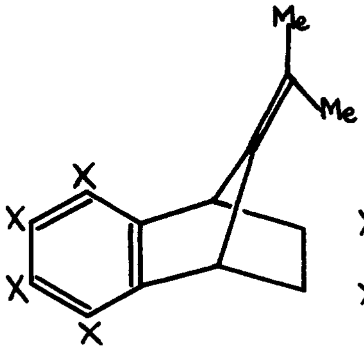
(Received in UK 7 June 1972; accepted for publication 16 June 1972)

While the pyrolysis of the epoxide (1; X=F, Y=O) leads to 1,2,3,4-tetrafluoronaphth-5-ol,[1] and that of the amino-analogue (1; X=H, Y=NH) affords α-naphthylamine,[2] the compound (1; X=F, Y=NMe) gives more complex results.[3] Interest in retro-Diels-Alder reactions[4] and in apparent similarities between mass spectral and thermal and photochemical processes[5] together with continued study of the chemistry of simple isoindoles[6] and isobenzofuran[7] prompts us to report certain of our own related results.

We were particularly interested in the question of the concertedness or otherwise of certain known[7b,d] retro-Diels-Alder reactions since the compounds (2; X=H or F) could each afford an isobenzofulvene[8] or a derivative of cyclopentindene. That *N*-methylisoindole[9] and isobenzofuran[7] are both relatively unstable is in accord with predictions,[10] but the fact that the tetrahalogeno-*o*-benzoquinones[11] are more stable than *o*-benzoquinone itself encouraged us to look for an increased stability in the systems studied.



(1)



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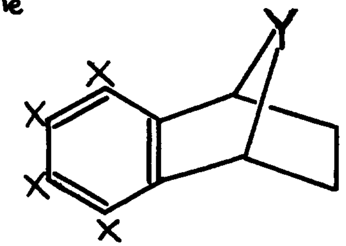

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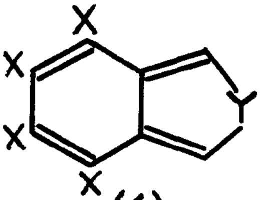

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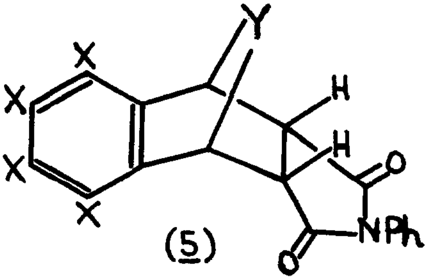

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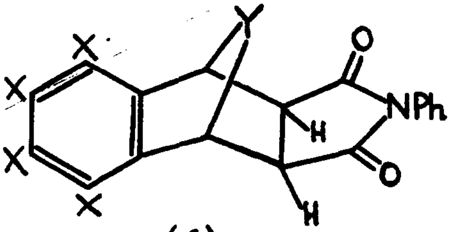

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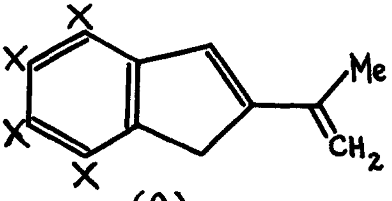

(9)

The mass spectra of the compounds (2; X=H or F) and (3; X=Clor F; Y=O or NMe) each show the loss of ethylene as the major mode of fragmentation of the molecular ions.[†] The compound (3; X=F, Y=NMe) loses ethylene when heated at 120°C for ca. 1 week in degassed ethanol or benzene to give a quantitative yield of 4,5,6,7-tetrafluoro-N-methylisoindole[‡] (4; X=F; Y=NMe).[§] The compound (4; X=F; Y=NMe) showed the expected diene reacticity with N-phenylmaleimide and at 120°C formed a 1:1 mixture of the endo- and exo-cycloadducts (5; X=F; Y=NMe) and (6; X=F; Y=NMe) reversibly. The compounds (3; X=Cl or F; Y=O) showed no tendency to form the isobenzofuran (4; X=Cl or F; Y=O) in solution and were recovered quantitatively after 1 week at 120°C. However, flow pyrolysis of (3; X=Cl or F; Y=O) at ca. 600°C and 0.3 mm in nitrogen[12] gave 4,5,6,7-tetrafluoroisobenzofuran (4; X=F; Y=O) and 4,5,6,7-tetrachloroisobenzofuran (4; X=Cl; Y=O) quantitatively. Spectral and other data indicate their stability to be greater than that of the parent compound.[*] Immediate reaction with N-phenylmaleimide at room temperature resulted in the

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[†] Supported by accurate mass measurements and the observation of the appropriate metastable peaks.

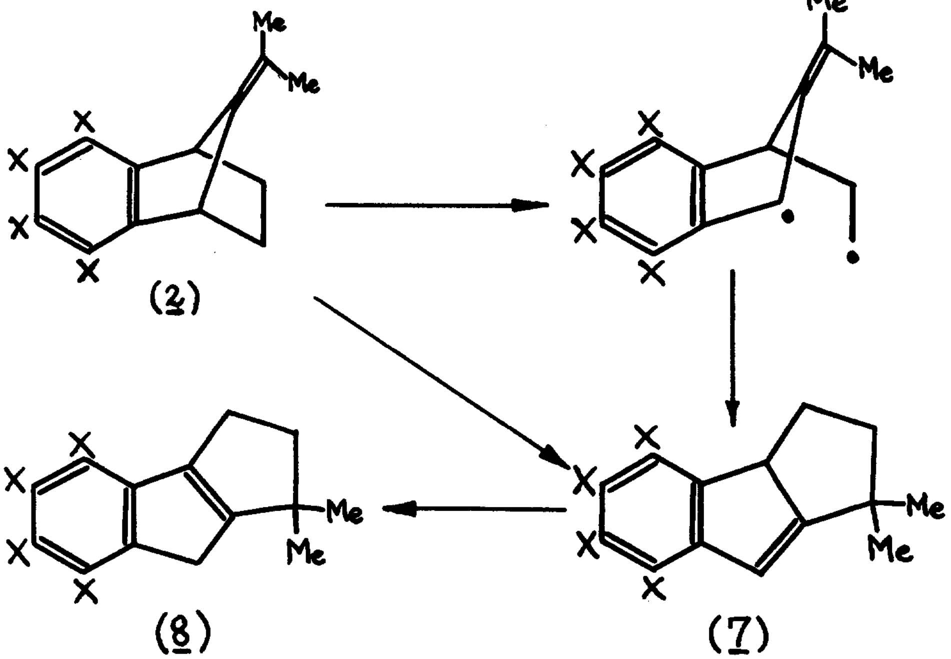
[‡] Satisfactory analytical and spectral data are available for this and other stable compounds.

[§] The high stability of (4; Y=NMe) is indicated by the fact that a crystalline sample has remained unchanged in the presence of air during six months. Dr.R.Kreher has informed us that the tetrachloro-analogue has a similar stability.

[*] A solution of (4; X=F; Y=O) (0.2 g. ml^{-1}) in deuteriochloroform at room temperature was stable for a prolonged period. The proton resonance signal had reduced to $\frac{1}{2}$ its initial area after 58 hr. An increased stability in these systems could be ascribed to a "push-pull" effect.

formation of 2:1 mixtures of the endo- and exo-adducts (5; X=Cl or F; Y=O) and (6; X=Cl or F; Y=O).

The flow pyrolysis of the compounds (2; X=H or F) at ca. 600°C at 0.3 mm each resulted in the formation of a mixture of products containing two major components. In a typical experiment the compound (8; X=H or F) was obtained in ca. 55% yield together with another compound (9; X=H or F[†]), in ca. 7% yield.



SCHEME

The Scheme shows possible mechanisms of formation of (8) which involve the initial formation of (7). The isomerisation of (7) to (8) is not unexpected in view of the known ease of isomerisation of indenes.[13] The fact that the isomerisation of (2) to (7) can occur by a symmetry allowed [1,3]sigmatropic shift[14] may perhaps suggest support for the implied view[7b,d] that stepwise retro-Diels-Alder reactions occur in carbon-bridged systems which do not have alternative symmetry allowed pathways.[‡] The formation of the compounds (9; X=H or F) may involve the inter-

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[†] This compound has not yet been obtained completely pure.

[‡] The dihydro-derivatives of (2) do not undergo the retro-diene reaction under identical conditions to those used for the pyrolysis of (2).

mediacy of isobenzofulvenes.[8]

We thank the S.R.C. and the Imperial Smelting Corporation for grants (to S.V.L. and A.P.P. respectively).

References

1. B.Hankinson, Ph.D. thesis, Loughborough, 1970.
2. L.A.Carpino and D.E.Barr, J.Org.Chem., 1966, 31, 764.
3. P.L.Coe and A.J.Uff, Tetrahedron, 1971, 27, 4065.
4. H.Kwart and K.King, Chem.Rev., 1968, 68, 415.
5. T.W.Bentley and R.A.W.Johnstone, Adv.Phys.Org.Chem., 1970, 8, 151;
   H.Heaney and A.P.Price, Chem.Comm., 1971, 894;
   R.Bloch, R.A.Marty, and P.de Mayo, J.Amer.Chem.Soc., 1971, 93, 3071.

6a) R.Kreher and J.Seubert, Z.Naturforsch., 1965, 20b, 75;
 b) J.Bornstein, D.A.McGowan, A.L.DiSalvo, J.E.Shields, and J.Kopecký, Chem.Comm., 1971, 1503;
 c) R.Bonnett and R.F.C.Brown, J.C.S.Chem.Comm., 1972, 393;
 d) B.Jacques and R.G.Wallace, ibid., 1972, 397.

7a) L.F.Fieser and M.J.Haddadin, Canad.J.Chem., 1965, 43, 1599;
 b) R.McCulloch, A.R.Rye, and D.Wege, Tetrahedron Letters, 1969, 5231;
 c) W.S.Wilson and R.N.Warrener, ibid., 1970, 5203;
 d) D.Wege, ibid., 1971, 2337;
 e) R.N.Warrener, J.Amer.Chem.Soc., 1971, 93, 2346;
 f) U.E.Wiersum and W.J.Mijs, J.C.S.Chem.Comm., 1972, 347.

8. ref. 8a in W.S.Wilson and R.N.Warrener, J.C.S.Chem.Comm., 1972, 211.
9. G.Wittig, H.Tenhaeff, W.Schoch, and G.Koenig, Annalen, 1951, 572, 1.
10. M.J.S.Dewar, A.J.Harget, N.Trinajstic and S.D.Worley, Tetrahedron, 1970, 26, 4505.
11. see for example M.F.Ansell, A.F.Gosden, V.J.Leslie, and R.A.Murray, J.Chem.Soc.(C), 1971, 1401.
12. J.A.Oliver and P.A.Ongley, Chem.and Ind., 1965, 1024.
13. J.A.Berson and G.B.Aspelin, Tetrahedron, 1964, 20, 2697;
    W.R.Roth, Tetrahedron Letters, 1964, 1009;
    J.Almy and D.J.Cram, J.Amer.Chem.Soc., 1970, 92, 4316.
14. R.B.Woodward and R.Hoffmann, Angew.Chem.Internat.Edn., 1969, 8, 781;
    J.A.Berson and G.L.Nelson, J.Amer.Chem.Soc., 1967, 89, 5503;
    J.A.Berson, Accounts Chem.Res., 1968, 1, 152.