Tetrahedron Letters Vol. 21, pp 4971 - 4972
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/1215-4971$02.00/0

PHENOXATHIINS FROM SPIROEPOXYCYCLOHEXADIENONES

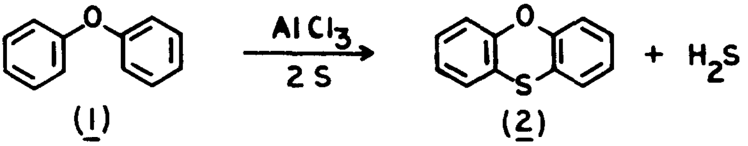
Jack E. Baldwin[‡], Paul Cacioli[#] and James A. Reiss[#*]

[‡]Dyson Perrins Laboratory, University of Oxford, Oxford OX1 3QY, U.K.

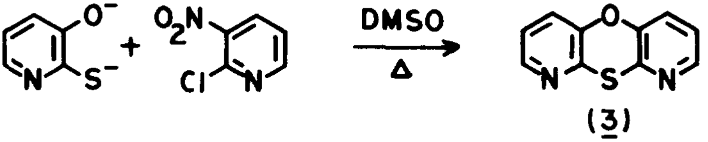
[#]Department of Organic Chemistry, La Trobe University, Bundoora,
Victoria 3083, Australia.

Summary: A series of phenoxathiins (7) were produced by the reaction between spiroepoxy-2,4-cyclohexadienones (5) and the pentachlorothiophenolate anion. The spiroepoxycyclohexadienones (5) may be regarded as polarity-reversed masked phenols in these reactions.

Recent reports[1,2] have shown an interest in the synthesis and properties of phenoxathiins and their aza analogues. Standard preparations of phenoxathiins are shown in Equations (1) and (2) for the parent compound (2)[3] and a dipyridophenoxathiin (3). The Ferrario reaction[3] for the cyclization of diphenylethers (Equation 1) has been used to produce a number of phenoxathiins but the presence of labile functional groups in the diphenyl (1) limits the scope of the reaction.



Equation 1

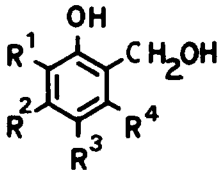


Equation 2

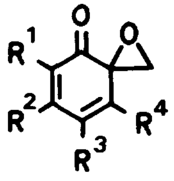
We have been investigating the chemistry of the spiroepoxy-2,4-cyclohexadienone ring system with nucleophiles and we wish to report some of our results on the synthesis of a series of highly substituted phenoxathiins.

The spiroepoxycyclohexadienones (5a-c) were prepared by the sodium periodate[4] (methanol) oxidation of the salicyl alcohols (4a-c). The spiroepoxy compounds (5a-c) on reaction with pentachlorothiophenol (6) under basic conditions (NaOH, EtOH, H_2O) gave the tetrachlorophenoxathiins (7a-c) in yields of 50-90%. The products were characterized by elemental analysis, ^{13}C and ^{1}H n.m.r. spectroscopy, and high resolution mass spectrometry.

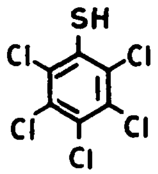
On reaction with p-chlorothiophenol in the presence of sodium hydroxide, the spiro compounds (5a-c) gave the anticipated 2-hydroxy-4'-chlorodiphenylsulphides (8a-c) together with formaldehyde which could be trapped as a dimedone adduct[5]. As these substitution products (7a-c and 8a-c) may be formally derived by substitution of the corresponding phenols under nucleophilic conditions, the spiroepoxycyclohexadienones may be regarded as masked phenols with reversed polarity.



(4a-c)



(5a-c)

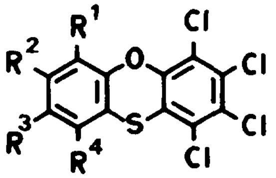


(6)

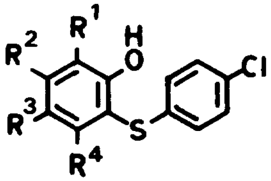
(a) $R^1 = R^3 =$ *t*-Bu; $R^2 = R^4 =$ H.

(b) $R^1 =$ *t*-Bu; $R^3 =$ Me; $R^2 = R^4 =$ H.

(c) $R^1 = R^2 = R^4 =$ Me; $R^3 =$ H.

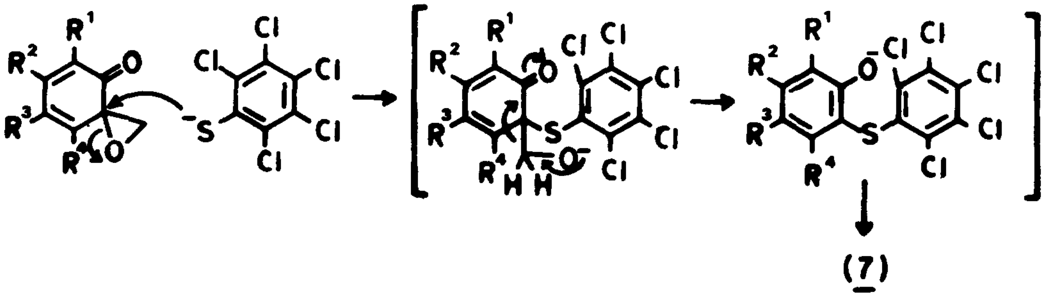


(7a-c)



(8a-c)

We envisage the mechanism of the reaction for the formation of the phenoxathiins proceeding as shown in Scheme 1 in which the first step is the nucleophilic displacement of the alkoxide at the quaternary spirocyclic carbon. A reverse aldol reaction followed by the intramolecular displacement of chloride would then produce the phenoxathiins.



Scheme 1

We are currently investigating reactions of these spiroepoxy compounds with other nucleophiles as possible pathways to novel heterocycles.

REFERENCES AND NOTES

1. G.E. Martin, J.D. Korp, J.C. Turley and I. Bernal, J. Heterocyclic Chem., **15**, 721 (1978).
2. J.S. Davies, K. Smith, J.R. Turner and G. Gymer, Tetrahedron Lett., **1979**, 5035.
3. D.S. Breslow and H. Skolnik, "Multi-sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles", John Wiley and Sons, New York, 1966; p. 864.
4. H.D. Becker, T. Bremholt and E. Adler, Tetrahedron Letts., **1972**, 4205.
5. E.C. Horning and M.G. Horning, J. Org. Chem., **11**, 95 (1946).

(Received in UK 10 October 1980)