Evidence for 1,2-Ketocarbenes in Thermolysis of Sodium *o*-Halogenophenoxides and for Benzothiirens in Thermolysis of Sodium *o*-Bromobenzenethiolates

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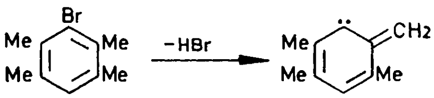
Summary Evidence for the intermediacy of a 1,2-ketocarbene in thermolysis of sodium *o*-bromophenoxide at 260° in alkyl benzenes to give dibenzo-*p*-dioxin is provided by trapping reactions with phenols, benzenethiols, and benzamide, benzoxiren being excluded by ^{13}C FT n.m.r. experiments, in contrast to the conversion of sodium *o*-bromobenzenethiolate into thianthrene, similarly shown to proceed *via* benzothiiren.

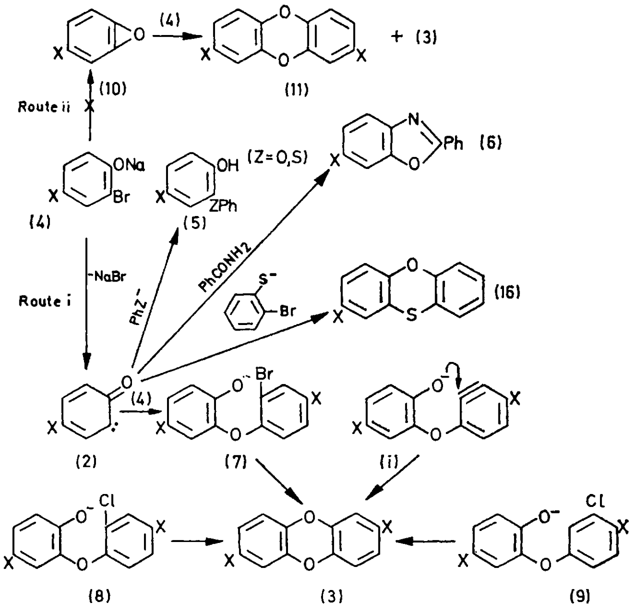
Following the successful 1,3-dehydrobromination of bromodurene *via* 1,2-methylenecarbenes[1] (**1**) it seemed that this approach might lead to the conversion of *o*-bromophenols into 1,2-ketocarbenes (**2**), and in this connection the somewhat neglected report[2] that thermolysis of sodium *o*-chlorophenoxide gives dibenzo-*p*-dioxin (**3**; X = H) was encouraging.



(1)

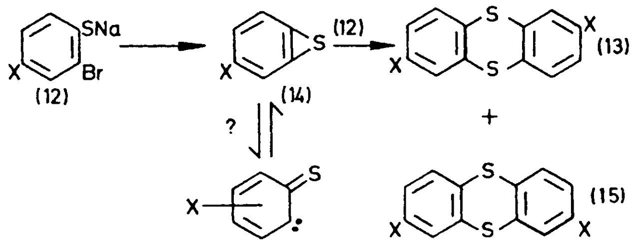
We now report evidence, based on trapping reactions with nucleophiles, which also have some synthetic use, supporting the intermediacy of ketocarbenes (**2**) in such reactions.

Thus sodium *o*-bromophenoxide (**4**; X = H) in mesitylene at 260° gave the dioxin (**3**; X = H; 45%), while in the presence of added sodium phenoxide or benzenethiolate, diversion to the diaryl ether (**5**; Z = O; X = H; 33%) or diaryl sulphide (**5**; Z = S, X = H; 44%) occurred. Evidence for the intermediacy of 1,3-dipoles in general has been frequently adduced from dipolar addition to benzonitrile, but in this case the expected benzoxazole (**6**; X = H) was formed (11%) only when the benzonitrile was wet. Control experiments showed that the trapping species was benzamide, formed by hydrolysis, an observation which might have significance in connection with the widespread



Scheme 1

use of benzonitrile as a 1,3-dipolarophile. These reactions are in accord with Scheme 1 whereby the ketocarbene (**2**) is intercepted by the various nucleophiles such as unchanged bromophenoxide (**4**) which gives an intermediate (**7**), which can react intramolecularly to give the observed dioxin (**3**), possibly, although not necessarily, *via* an aryne (route i). In accord with this, however, both the 2- and 3-chlorophenoxides (**8**; X = H) and (**9**; X = H) gave the dioxin (**3**; X = H).



Scheme 2

We discount routes involving nucleophilic attack on unchanged *o*-bromophenoxide ion and also that involving the intermediacy of benzoxirens (**10**) (route ii), the latter because both 4- and 5-methyl-2-bromophenoxide, separately, gave isomerically pure 2,7-dimethyldibenzo-*p*-dioxin (**3**; X = Me), as shown by ^{13}C FT magnetic resonance. An isomeric mixture of the 2,7- and 2,8-dimethyl derivatives (**3** and **11**; X = Me) would have been expected from the oxiren (**10**), control experiments using a mixture of 4- and 5-methyl-2-bromophenoxides having given such a mixture, clearly defined by the ^{13}C FT magnetic resonance technique.

We discount direct nucleophilic attack on unchanged *o*-bromophenoxide both intuitively, because attack by one negative ion on another is unlikely, and because in the much more favourable case of 2-phenoxybromobenzene no reaction occurred with either sodium phenoxide or sodium *o*-methoxyphenoxide.

We also report that thermolysis of the corresponding sodium *o*-bromobenzenethiolate (**12**; X = H) proceeds very cleanly to give thianthrene (**13**; X = H; 41%) but in contrast to the oxygen analogue, and due presumably to the greater polarisability and size of sulphur compared with oxygen, this appears to proceed *via* the benzothiiren (**14**; X = H) rather than the 1,2-thioxocarbene. This follows from the observation that sodium 2-bromo-4-methylbenzenethiolate (**12**; X = Me) gives a mixture (58%) of thianthrenes shown by ^{13}C FT magnetic resonance to consist of two isomeric dimethylthianthrenes (**15** and **13**; X = Me) in comparable amounts rather than the 2,7-dimethyl isomer (**13**; X = Me), which alone would have been expected from reaction of the 1,2-thioxocarbene (Scheme 2).

In accord with the foregoing a mixture of sodium *o*-bromophenoxide and benzenethiolate gave a mixture of thianthrene (**13** X = H; 16%) and phenoxathiin (**16**; X = H; 28%).

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[1] J. I. G. Cadogan, J. K. A. Hall, A. K. Robertson, and J. T. Sharp, *Chem. Comm.*, 1971, 1273.

[2] F. Baeyer, 1909, G.P.223,367 (*Chem. Abs.*, P42981.^{4})