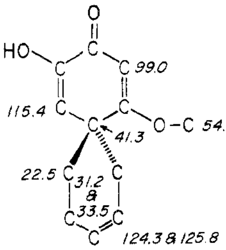

Figure 2.

The formation of **10**, though not predicted, can be rationalized in terms of cycloaddition of **2a** with 1,3-butadiene. Intermediate **2a** must arise by tautomerization of **2**. The tautomerization of an *o*-benzoquinone to a 2-hydroxy-4-methylenecyclohexadienone, followed by cycloaddition of the latter at the exocyclic methylene group, is to our knowledge a new route to spiro systems.

Some rather subtle structural features are exercising strong control over the choice of the options of conventional cycloadditon (*cf.* **1** → **9**) *vs.* enolization–cycloaddition (*cf.* **2** → **10**).[12] These factors have not, at this point, been defined.

Synthetic applications of Diels–Alder reactions of o-benzoquinones will be described in due course.

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Supplementary Material Available. The experimental procedures for the reactions described in this investigation will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3610.

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(4) To our knowledge there are only two examples of a 4-methoxy-*o*-benzoquinone acting in a dienophilic capacity. These were reported on the parent 4-methoxy-*o*-benzoquinone with cyclopentadiene[5a] and with 2,3-dimethyl-1,3-butadiene.[5b] Neither case is necessarily suggestive of the deactivating effect of the 4-methoxyl group on the dienophilicity of the 3,4 double bond since the cycloaddition at the 5,6 double bond may be rationalized in purely steric terms. The case of quinone **1**, described here, is the first one involving a 5-substituted 4-methoxy system. The exclusive dienophilicity of the 5,6 double bond and the stability required to allow for cycloaddition with 1,3-butadiene are most readily rationalized on the basis of the effects of the 4-methoxy group on both the diene and dienophilic properties postulated above.

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(11) The only two previous examples of the condensation of the relatively nonreactive 1,3-butadiene with *o*-benzoquinones were cases involving a 4-carbomethoxyl[5b] or a 4-cyano group.[5b] Such groups are known[3] to enhance dienophilicity.

(12) Although we do not have a full accounting of the material in either the reaction of **1** or **2** with butadiene, we believe that there is very little, if any, spiro product in the case of **1** of fused product in the case of **2**. Tlc analysis of the mother liquors in the reaction of **1**, where a 63% yield of crystalline **9** was obtained, shows additional **9** and variety of other spots. While these have not been identified, it is not likely that any one is present to the extent of more than a few per cent. In the case of **2**, where a 48% yield of crystalline **8** was obtained, the major loss, 20–25%, arises from a red, intractible substance. The mother liquors after separation of crystalline **10**, show (tlc analysis) additional amounts of **10** and several other unidentified spots. The nmr spectrum of these mother liquors does not show any methyl resonance in the region δ 1–1.5 where it would be expected from the direct cycloaddition of **2** with 1,3-butadiene.

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"Nucleophilic" Replacement of Two Halogens in Dihalobenzenes without the Intermediacy of Monosubstitution Products[1]

Summary: The fact that several dihalobenzenes react with thiophenoxide ion in ammonia under irradiation to form disubstitution products without substantial intermediacy of monosubstitution products constitutes unique evidence of mechanism, serving to exclude numerous possibilities, but straightforwardly accommodated by the SRN1 mechanism.

Sir: Aryl iodides react readily with thiophenoxide ion in liquid ammonia, under irradiation, to form diaryl sulfides in high yield[2] (eq 1). We now report that under the same conditions many dihalobenzenes afford disubstitution products. Typically, little if any monosubstitution product is formed. Moreover, we have evidence that for the most part *the monosubstitution product is not an intermediate in the production of disubstitution product.*

$$\mathrm{ArI} + \mathrm{PhS}^- \xrightarrow{h\nu} \mathrm{Ar{-}S{-}Ph} + \mathrm{I}^- \qquad (1)$$

A representative reaction is that of *m*-chloroiodobenzene with thiophenoxide ion during 2.5-hr irradiation with Pyrex-filtered light to form the bis sulfide, *m*-di(thiophenoxy)benzene, in 91% yield accompanied by a mere trace of *m*-chlorophenyl phenyl sulfide. Even at short reaction times, at which the dihalobenzene is but partially reacted, only a trace of monosubstitution is observable alongside predominant disubstitution.

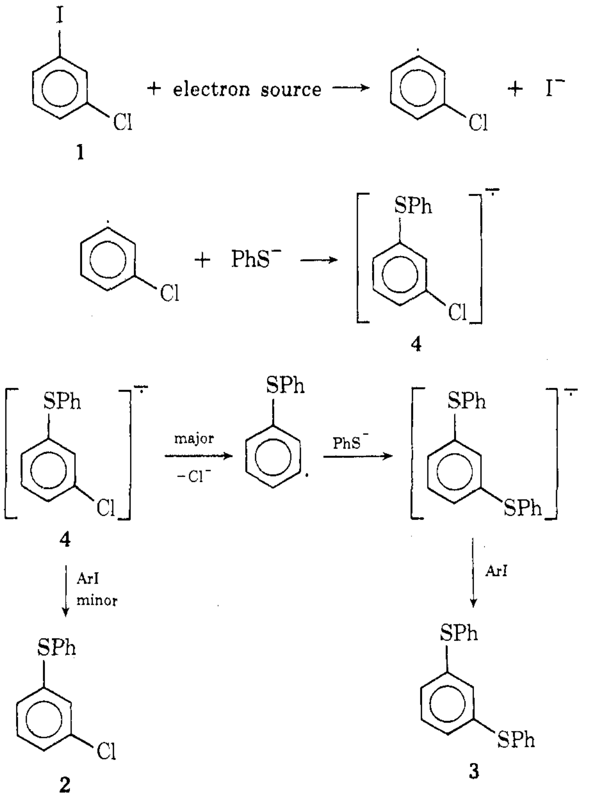
The results of numerous experiments are summarized in Table I. It is noteworthy that *m*-fluoroiodobenzene (run 8) underwent only replacement of iodine, yielding 96% of *m*-fluorophenyl phenyl sulfide. However, in *p*-iodophenyltrimethylammonium ion (run 6) both the iodine and the trimethylammonio group were replaced, forming the bis sulfide in 95% yield. Replacement of the trimethylammonio substituent in aromatic SRN1 reactions is a familiar phenomenon.[3–5]

Table I
Photostimulated Reactions of Aryl Halides with Thiophenoxide Ion[a] in Liquid Ammonia

Run no.	Substrate	Reaction time, min	Sulfide product	% yield[b]	Other products[c]
1	*m*-ClC_6H_4I	150	*m*-$PhSC_6H_4SPh$	91	PhSPh, *m*-ClC_6H_4SPh
2	*p*-ClC_6H_4I	120	*p*-$PhSC_6H_4SPh$	89[e]	PhSPh, *p*-ClC_6H_4SPh
3	*m*-BrC_6H_4Br	190	*m*-$PhSC_6H_4SPh$	92	PhSPh
4	*m*-ClC_6H_4Br	180	*m*-$PhSC_6H_4SPh$	55[f]	PhSPh, *m*-ClC_6H_4SPh
5	*p*-BrC_6H_4Br	300	*p*-$PhSC_6H_4SPh$	64[d,g]	
6	*p*-$IC_6H_4N^+Me_3I^-$	180	*p*-$PhSC_6H_4SPh$	95	PhSPh
7	*o*-ClC_6H_4I	90	*o*-$PhSC_6H_4SPh$	77[h]	PhSPh, *o*-ClC_6H_4SPh
8	*m*-FC_6H_4I	100	*m*-FC_6H_4SPh	96	

[a] PhS^- supplied by dissolving PhSH in ammonia; irradiation by "350 nm" lamps.[3] [b] Isolated yield unless otherwise indicated. [c] Trace amounts. [d] Glpc yield. [e] After recrystallization. [f] 33% unreacted *m*-chlorobromobenzene. [g] 26% unreacted *p*-dibromobenzene. [h] 9% unreacted *o*-chloroiodobenzene.

Scheme I



Kinetic analysis of the photostimulated reaction of *m*-chloroiodobenzene (1) with thiophenoxide ion shows that, except to a minor extent, the monosubstitution product (2) is not an intermediate in formation of bis-sulfide 3. First, in separate reactions with thiophenoxide ion, 1 is more reactive than 2. Thus, during 105 sec irradiation, 1 reacted to the extent of 68% but 2 only to the extent of 15%, both to form predominantly 3. Second, when mixtures of 1 or 2 and iodobenzene were allowed to compete for excess thiophenoxide, iodobenzene was found to be more reactive than 2 but less reactive than 1. Third, in direct competition between 1 and 2 for thiophenoxide ion, 1 was 17.4 times more reactive than 2.

These relative reactivity measurements show that 2 is too unreactive to participate as a major reaction intermediate.

That monosubstitution product 2 is, in the main, not an intermediate en route to disubstitution product 3 is a strange result, and constitutes powerful evidence of mechanism. It serves to exclude numerous conceivable mechanisms of substitution. On the other hand, the previously proposed SRN1 mechanism[2,6] not only accommodates this result, but leads to an expectation of it. That mechanism, adapted to the present case, is sketched in Scheme I.

In Scheme I, the fate of radical anion 4 is of central interest. Loss of chloride ion from 4 is the major pathway and leads to disubstitution product 3 without the intervention of 2. Loss of an electron from 4, presumably by transfer to 1, forms 2 but is apparently a minor pathway.

The fact that *m*-fluoroiodobenzene (run 8) gave only monosubstituted product indicates that the analogous *m*-fluorophenyl phenyl sulfide radical anion preferentially transfers an electron to aryl iodide. C–F bonds are more difficult to break than C–Cl bonds.

The mechanism of Scheme I is the only one conceivable to us that accommodates the strange result we report. We must, however, add the universal proviso that a presently inconceivable mechanism may also accommodate the evidence.

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Photostimulated Condensation of Aryl Iodides with Potassium Dialkyl Phosphites to Form Dialkyl Arylphosphonates[1]

Summary: Aryl iodides react rapidly with potassium dialkyl phosphites, $(RO)_2PO^-K^+$, in liquid ammonia under "350-nm" irradiation to form dialkyl arylphosphonates in 87–96% yields, probably by the SRN1 mechanism.

Sir: We have found that potassium salts of dialkyl phosphites react rapidly with aryl iodides in liquid ammonia under Pyrex-filtered irradiation to form dialkyl esters of arylphosphonic acids in nearly quantitative yields (Scheme I).