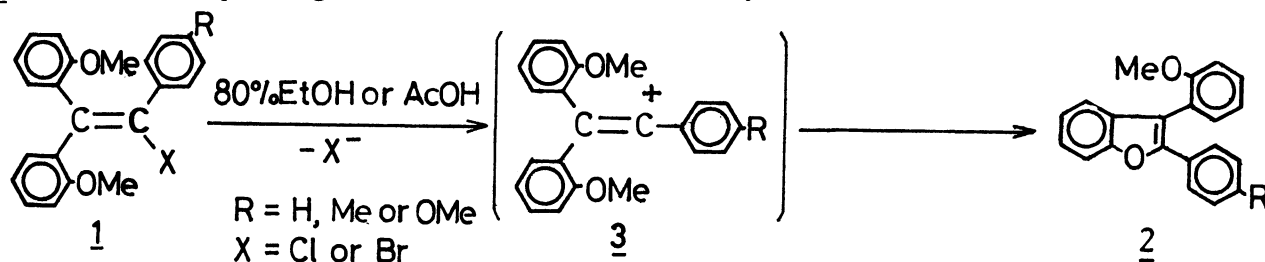


SILVER ION-ASSISTED INTRAMOLECULAR NUCLEOPHILIC ADDITION-ELIMINATION
OF VINYL BROMIDES; FORMATION OF BENZOTHIOPHENES
FROM 2-(o-METHYLTHIOPHENYL)VINYL BROMIDES

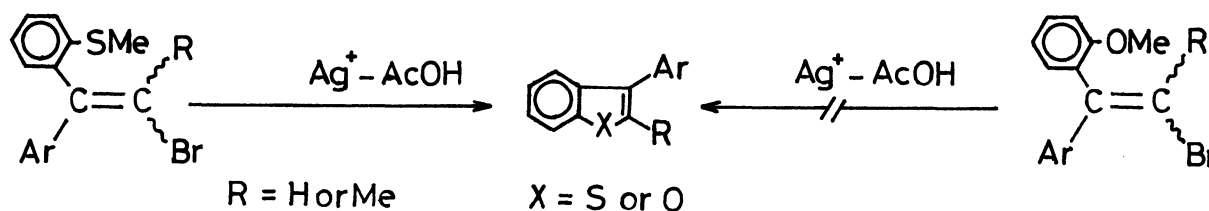
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The reactions of 1-unsubstituted and 1-methyl-2-(o-methylthio-phenyl)vinyl bromides in acetic acid in the presence of silver salt gave exclusively benzothiophenes, while the corresponding 2-methoxy-phenyl analogues were unreactive under similar conditions. This cyclization is considered to involve an intramolecular nucleophilic attack of the sulfur atom at the carbon atom of the double bond activated by the silver ion with the elimination of the silver bromide.

Recently we found that the reactions of 2,2-bis(o-methoxyphenyl)-1-arylvinyl halides 1 under solvolytic conditions exclusively gave benzofurans 2 via vinyl cations 3¹⁾. The corresponding 1-unsubstituted and 1-methyl derivatives are found to be

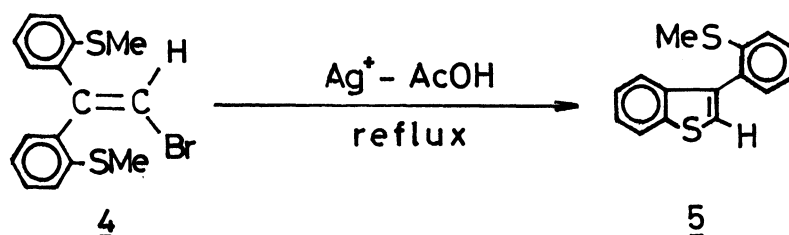


unreactive even in the presence of silver salt, as will be described below. Such a difference in reactivity is well recognized in the solvolysis of vinyl halides²⁾. Here we want to report that in the presence of silver salt 2-(o-methylthiophenyl)vinyl bromides gave benzothiophenes exclusively even in the cases of 1-unsubstituted and 1-methyl derivatives.



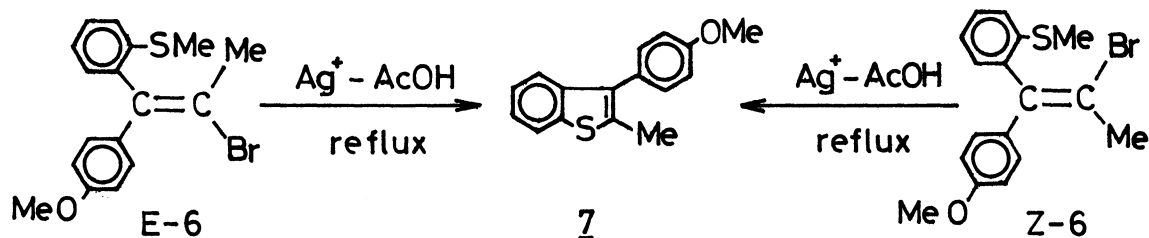
2,2-Bis(o-methylthiophenyl)vinyl bromide 4³⁾ was treated with one equivalent of silver acetate⁴⁾ in acetic acid under refluxing for 18 hours. The nmr spectrum of the reaction mixture showed three singlet signals of methylthio group. Two of them at δ

2.37 and 2.40 were identical with those of the starting material 4 and the other signal at δ 2.27 was assigned to that of 3-(o-methylthiophenyl)benzothiophene 5. From the nmr spectrum the conversion was calculated to be 48%. The further refluxing of this reaction mixture with excess of silver acetate in acetic acid for 38 hours gave 5

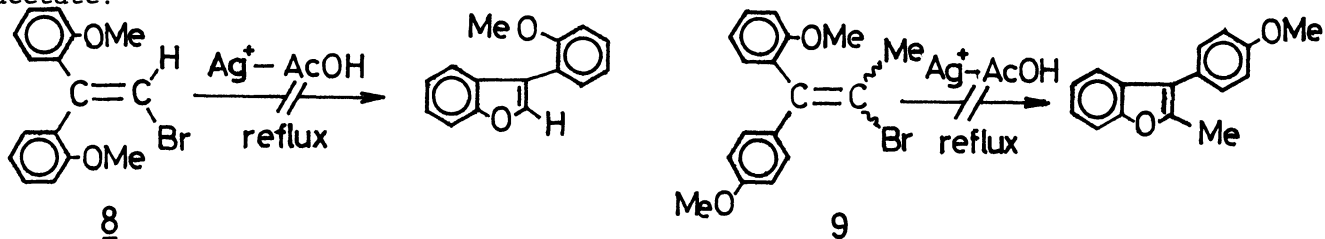


as the sole product (82% conversion). White crystals were isolated by alumina chromatography and identified as 5³⁾. The cyclization of 4 did not proceed without silver salt under refluxing in acetic acid for 24 hours.

Similarly, a 1:1 mixture of E- and Z-1-(p-methoxyphenyl)-1-(o-methylthiophenyl)-2-bromopropene 6³⁾ was treated with 1.5 equivalents of silver acetate in acetic acid under refluxing for one hour (45% conversion). 3-(p-Methoxyphenyl)-2-methylbenzothiophene 7³⁾ was exclusively formed. When both the reactions of a 1:1 mixture and a 3:7 (or 7:3) mixture of E-6 and Z-6 were interrupted, the E/Z ratios of 6 remained unchanged, respectively. These results show that the cyclization of 6 occurs more easily than that of 4 and that there are no large difference in reactivity and no isomerization between E- and Z-isomers of 6.



On the other hand, the corresponding oxygen analogues, 2,2-bis(o-methoxyphenyl)-vinyl bromide 8³⁾ and 1-(o-methoxyphenyl)-1-(p-methoxyphenyl)-2-bromopropene 9³⁾ were unreactive under similar or siverer conditions. 8 was treated with 6 equivalents of silver trifluoroacetate in acetic acid under refluxing for two days, but the starting material 8 was recovered unchanged. Similarly, a 1:1 mixture of E-9 and Z-9 was recovered unchanged after 11-hour refluxing in acetic acid with 10 equivalents of silver acetate.



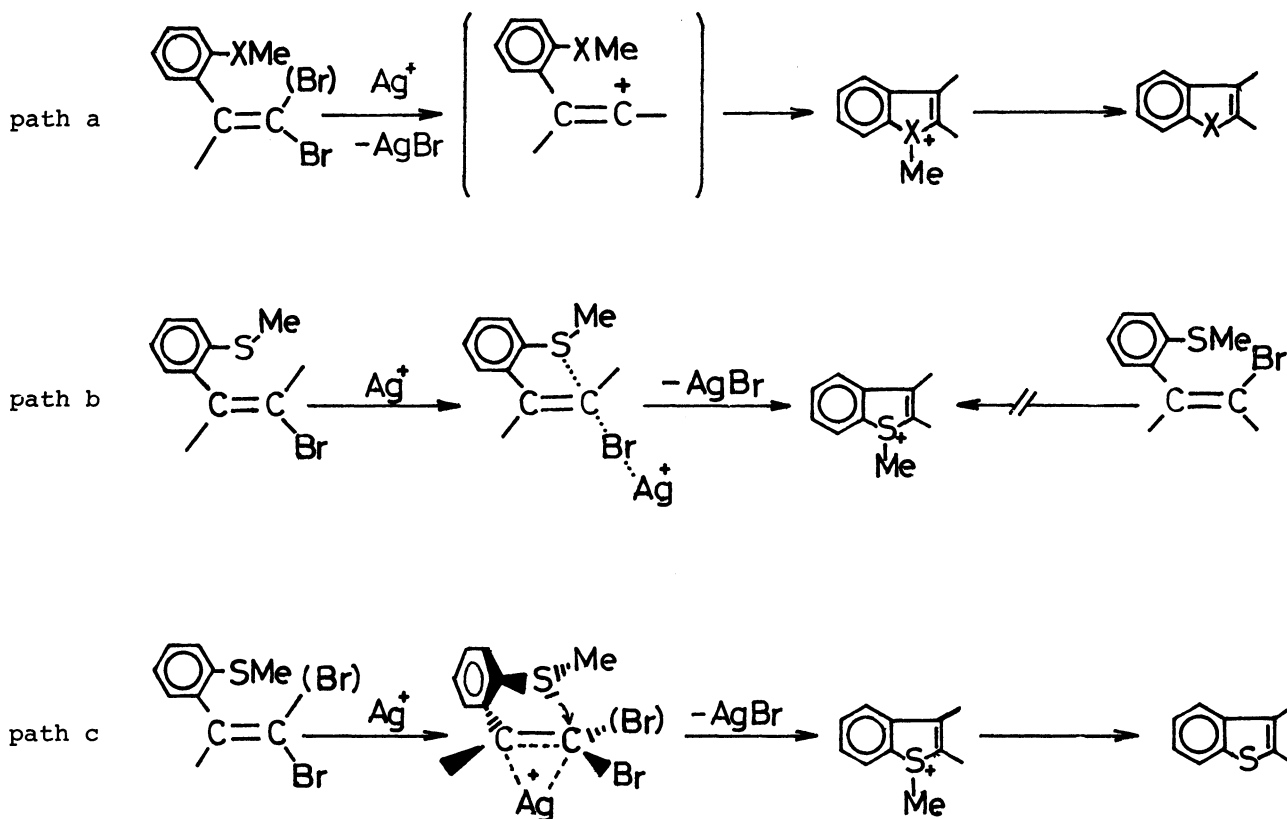
This cyclization was observed in another solvent system. The n-hexane solution of 4 was refluxed for 23 hours in the presence of 3 equivalents of suspension silver trifluoroacetate (34% conversion), and benzothiophene 5 was formed as the sole product. The corresponding oxygen analogue 8 was recovered unchanged after 6-day

refluxing in n-hexane with 6 equivalents of silver trifluoroacetate.

Consequently, this cyclization is characteristic of the sulfur derivatives (4 and 6) and occurs in the presence of silver salt.

If we were to suppose that the cyclization of 4 and 6 proceeded via the vinyl cation⁵⁾ (path a), then we would not be able to conceive why the methoxy analogues 8 and 9 did not cyclize; for there seem to be little a priori difference between the 2-(o-methylthiophenyl)vinyl and the 2-(o-methoxyphenyl)vinyl bromides in the tendencies to ionize⁶⁾ unless some anchimeric assistance were operating only in the former case. The presence of such anchimeric acceleration of ionization⁷⁾ (path b) can be ruled out because E-6 and Z-6 cyclize at approximately the same rate.

It is considered that this cyclization is a sort of intramolecular nucleophilic addition-elimination⁸⁾ (path c). The nature of silver ion forming a charge transfer complex with π -electron of olefins⁹⁾ and aromatics¹⁰⁾ is taken into consideration in addition to its affinity for halogen atoms. Some positive charge may develop on the olefinic carbons as a charge transfer complex is formed. The sulfur atom attacks at the activated π -orbital of the double bond with the elimination of the silver bromide. This attack may cause no large rate difference between the geometrical isomers. The large element effect observed with the sulfur and the oxygen atoms is the result of the more facile attack of the sulfur atom, which is caused by its higher nucleophilicity and a more suitable distance between the sulfur atom and the reaction center for cyclization. This mechanism is, therefore, most likely for this cyclization.



R E F E R E N C E S and N O T E S

1. T.Sonoda, S.Kobayashi, and H.Taniguchi, unpublished results.
2. For a recent and clear review for solvolysis of vinyl derivatives, see L.R. Subramanian and M.Hanack, *J.Chem.Educ.*, 52,80(1975).
3. The structures of vinyl bromides 4, 6, 8, and 9, which were prepared by bromination of the corresponding ethylenes in CCl_4 or $\text{CCl}_4\text{-CH}_2\text{Cl}_2$, and benzothiophenes 5 and 7 were assigned by the following analyses and spectra.
 - 4: mp 110-111°C: Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{S}_2\text{Br}$: C,54.70; H,4.30. Found: C,54.69; H, 4.29: mass: no M^+ , 271($\text{M}^+\text{-Br}$): uv(cyclohexane) λ_{max} 245nm(log ϵ 4.32), 229(4.36): nmr(CCl_4) δ 2.36(s,SCH₃), 2.40(s,SCH₃), 6.75(s,=CH-), 6.9-7.4(m,arom.H).
 - 5: mp 83.5-84°C: Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{S}_2$: C,70.37; H,4.72. Found: C,70.04; H,4.69: mass: 256(M^+): uv(cyclohexane) λ_{max} 300nm(log ϵ 3.72), 290(3.72), 255(4.14): nmr(CCl_4) δ 2.27(s,SCH₃), 7.1-7.9(m,arom.H).
 - 6: it has not been separated into each of E- and Z-6 and their geometrical structures have not been determined: a 1:1 mixture was obtained in bromination in CCl_4 , and a 3:7(or 7:3) one in $\text{CCl}_4\text{-CH}_2\text{Cl}_2$ (11:1). nmr(CCl_4) δ 2.20 and 2.30(two s,SCH₃ and CH₃ of E(or Z)-6), 2.30 and 2.47(two s, SCH₃ and CH₃ of Z(or E)-6), 3.67(s,OCH₃ of E-6 and Z-6), 6.6-7.3(m,arom.H).
 - 7: mp 109°C: Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{OS}$: C,75.56; H,5.55. Found: C,75.07; H,5.47: mass: 254(M^+): uv(cyclohexane) λ_{max} 302nm(log ϵ 3.76), 292(3.81), 263(4.10), 235 (4.61): nmr(CCl_4) δ 2.43(s,CH₃), 3.77(s,OCH₃), 6.7-7.7(m,arom.H).
 - 8: mp 116.5-117.5°C(lit. mp 114-116°C; G.Köbrich, H.Trapp, K.Flory, and W.Drischel, *Chem.Ber.*, 99,689(1966)).
 - 9: a 1:1 mixture of E- and Z-9: nmr(CCl_4) δ 2.23 and 2.42(two s,CH₃ of E- and Z-9), 3.70(s,OCH₃ of E- and Z-9), 6.6-7.3(m,arom.H).
4. A similar result was obtained by use of silver trifluoroacetate; 4 was treated with 3.4 equivalents of the silver salt in acetic acid under refluxing for 21 hours (54% conversion). 5 was formed exclusively.
5. Solvolysis of 1-unsubstituted and 1-methylvinyl bromides via vinyl cations has not yet been observed. See ref.2.
6. It is well known that in solvolysis of vinyl derivatives 2-aryl substituent effect is not so much important as 1-aryl one. See L.L.Miller and D.A.Kaufman, *J.Amer. Chem.Soc.*, 90,7282(1968).
7. An anchimeric acceleration by a sulfur atom in solvolysis of vinyl derivatives was reported in the case of 3-methylthio-2-butenyl trinitrobenzenesulfonate; A. Burighel, G.Modena, and U.Tonellato, *Chem.Comm.*, 1325(1971) and earlier ref..
8. S.Patai and Z.Rappoport in "The Chemistry of Alkenes", S.Patai,Ed., Interscience, London, 1964,p.469: G.Modena, *Accounts, Chem.Res.*, 4,73(1971).
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