Formation of the Benzofuran, Benzothiophen, and *N*-Methylindole Ring Systems *via* Vinyl Cations

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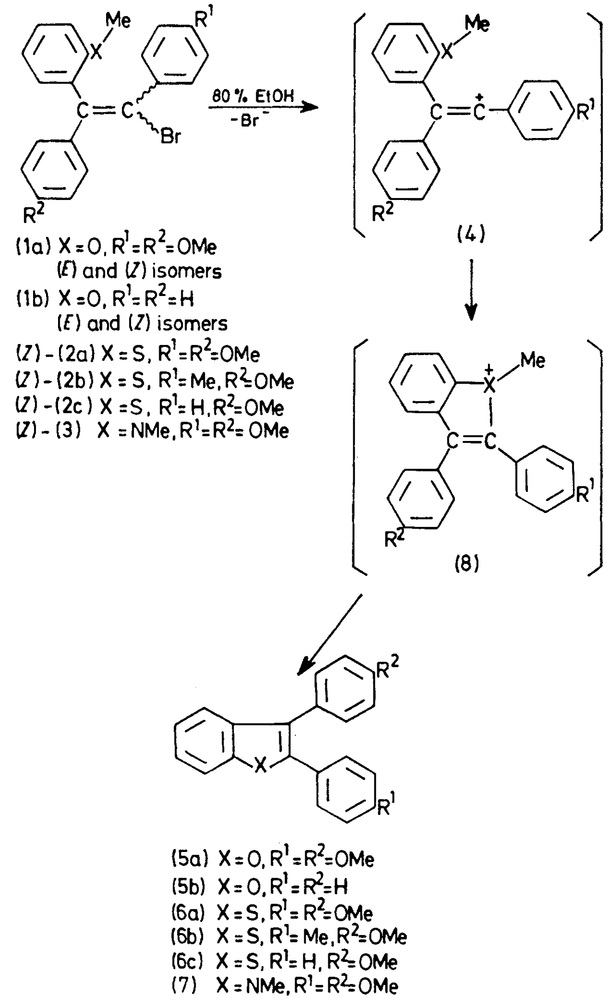
Summary Reactions of the vinyl bromides (**1**), (**2**), and (**3**), containing O, S, and N atoms at the *ortho* position of the β-aryl substituents, in 80% EtOH gave (**5**), (**6**), and (**7**), respectively, *via* the vinyl cations (**4**).

Although the existence of vinyl cations has gained general acceptance in the solvolysis of vinyl derivatives,[1] their use in syntheses is limited[2] despite a growing interest in such species. We now report that under solvolytic conditions α-arylvinyl bromides containing β-*o*-methoxyphenyl (**1**), β-*o*-methylthiophenyl (**2**), and β-*o*-*NN*-dimethylaminophenyl (**3**) groups undergo, *via* the vinyl cations (**4**), selective cyclisation to benzofuran (**5**), benzothiophen (**6**), and *N*-methylindole (**7**) derivatives, respectively.

The reaction of the vinyl bromide (*E*)-(**1a**) in basic (3·3 equiv. of NaOH) 80% EtOH at 120 °C for 8 h gave 2,3-bis-(*p*-methoxyphenyl)benzofuran (**5a**) quantitatively. Similarly, the vinyl bromides (**1b**), (**2a**—**c**), and (**3**) in aqueous EtOH with excess of NaOH or in AcOH with AgOAc resulted in the exclusive formation of (**5b**), (**6a**—**c**), and (**7**), respectively.†

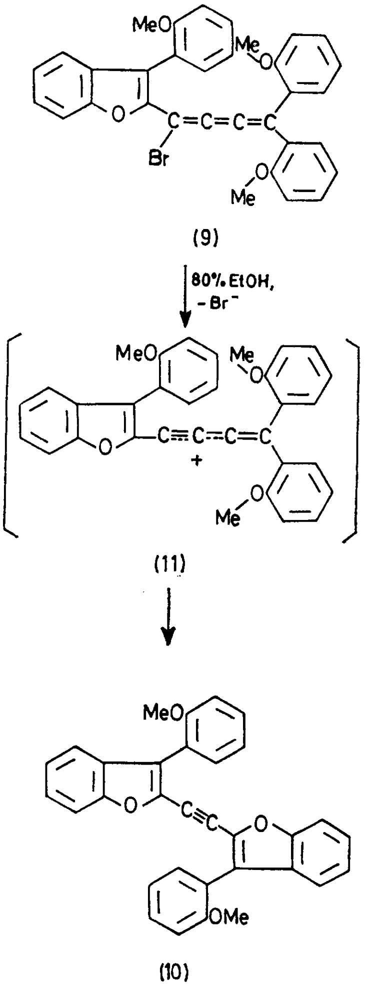


(1a) X = O, $R^1 = R^2 = OMe$
(*E*) and (*Z*) isomers
(1b) X = O, $R^1 = R^2 = H$
(*E*) and (*Z*) isomers
(*Z*)-(2a) X = S, $R^1 = R^2 = OMe$
(*Z*)-(2b) X = S, $R^1 = Me$, $R^2 = OMe$
(*Z*)-(2c) X = S, $R^1 = H$, $R^2 = OMe$
(*Z*)-(3) X = NMe, $R^1 = R^2 = OMe$

(4)

(8)

(5a) X = O, $R^1 = R^2 = OMe$
(5b) X = O, $R^1 = R^2 = H$
(6a) X = S, $R^1 = R^2 = OMe$
(6b) X = S, $R^1 = Me$, $R^2 = OMe$
(6c) X = S, $R^1 = H$, $R^2 = OMe$
(7) X = NMe, $R^1 = R^2 = OMe$



(9)

(11)

(10)

A kinetic study of the reactions of the vinyl bromides showed: (a) first-order reaction rates [k_1 for (*E*)-(**1a**) $2{\cdot}85 \times 10^{-4}$ s^{-1}, k_1 for (*Z*)-(**1a**) $3{\cdot}82 \times 10^{-4}$ s^{-1}, and k_1 for (**2a**) $0{\cdot}59 \times 10^{-4}$ s^{-1} in basic 80% EtOH at 120 °C], (b) solvent polarity effects [*m* 0·49 for (*E*)-(**1a**), 0·48 for (*Z*)-(**1a**) and 0·53 for (**2a**) at 120 °C], (c) large α-substituent effect [k_1(**2a**)/k_1(**2b**) 65 in 50% EtOH at 160 °C], and (d) activation parameters [$\Delta H^{\ddagger}$ 25·3 kcal mol^{-1}, $\Delta S^{\ddagger}$ −11 cal K^{-1} mol^{-1} at 120 °C for (*E*)-(**1a**)] which are similar to those for reactions for which the S_N1 mechanism has been established.[1] These results indicate that these cyclisations proceed by an S_N1 mechanism *via* the vinyl cations (**4**), which are attacked by the β-*ortho*-substituents to form the five-membered onium ions (**8**), followed by the elimination of Me to give (**5**), (**6**), and (**7**).

The onium ion (**8**) could be trapped as its perchlorate in the case of (**3**). The reaction of (**3**) in 70% EtOH with 1 equiv. of $AgClO_4$ at room temperature for 3 h gave the indolium perchlorate (**8**; X = NMe, $R^1 = R^2 = OMe$) (33% yield), m.p. 206—207 °C,† which was converted into the indole (**7**) on treatment with excess of NaOH in EtOH–tetrahydrofuran (1 : 1).[3]

In the solvolysis of the butatrienyl bromide (**9**) in 80% EtOH a similar cyclization to the bis(benzofuranyl)acetylene (**10**) *via* the cation (**11**) was observed.

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† All new compounds reported here gave satisfactory analyses and spectra.

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