

SYNTHESIS AND REACTIVITY OF
1,2-DIARYL-2-ARYLMERCAPTOVINYL 2,4,6-TRINITROBENZENESULFONATES

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(Received in UK 4 April 1968; accepted for publication 19 June 1968)

Following our previous research on the addition of sulfenyl chlorides to acetylenes (1,2), we undertook the study of the addition of other sulfenyl derivatives to the triple bond. We wish to communicate some preliminary results obtained in the addition of arylsulfenyl 2,4,6-trinitrobenzenesulfonates to toluene and 4,4'-dimethyltoluene.

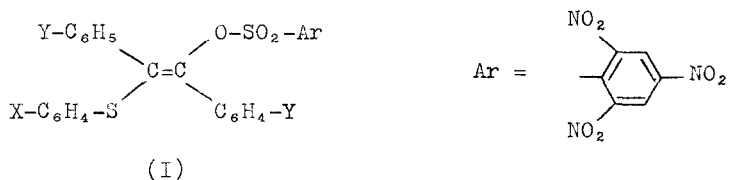
The arylsulfenyl 2,4,6-trinitrobenzenesulfonates were formed by reaction in CH_2Cl_2 of various arylsulfenyl chlorides with silver 2,4,6-trinitrobenzenesulfonate following a procedure similar to that described by Pettitt and Helmkamp (3,4). They were treated directly in the same solvent with toluene and 4,4'-dimethyltoluene at about -25° . The temperature was then allowed to rise gradually to room temperature.

Quick filtration of the insoluble AgCl followed by addition of pentane to the clear solution resulted in the precipitation of orange-red crystalline solids, which were purified by recrystallization from methylene chloride-pentane or chloroform-pentane.

The analytical data (5) for the compounds obtained were consistent with 1:1 adducts of arylsulfenyl 2,4,6-trinitrobenzenesulfonates and toluene or 4,4'-dimethyltoluene respectively. These adducts are characterized by a weak absorption band at 400-420 $\text{m}\mu$. On the basis of the i.r. spectrum [absence of the two strong bands at 1208 and 1057 cm^{-1} , indicative of an ionic sulfonate (2)], the NMR spectrum of the adduct of phenylsulfenyl 2,4,6-trinitrobenzenesulfonate and 4,4'-dimethyltoluene (two singlets for the two methyl groups) and chemical reactivity the adducts must be considered covalent compounds and are formulated as 1,2-diaryl-2-arylmecaptovinyl 2,4,6-trinitrobenzenesulfonates I.

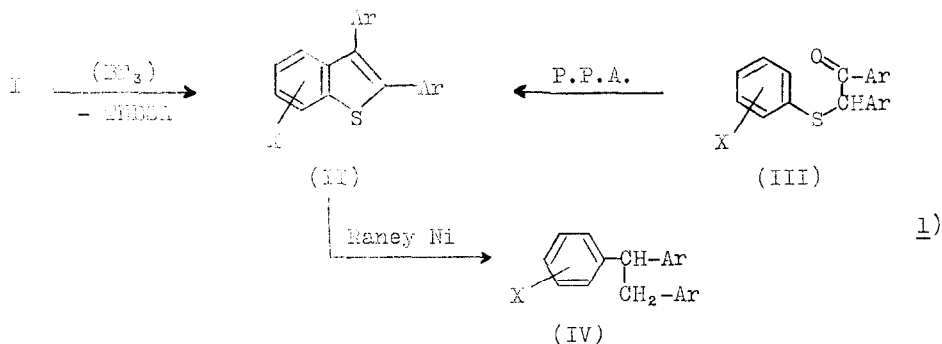
The trans structure is not yet proved but is suggested by analogy with similar addition reactions, the stereochemistry of which is known (6).

The adducts I decompose spontaneously when dissolved in inert solvents (CH_2Cl_2 , CHCl_3 , CH_3NO_2) as shown by the disappearance of the characteristic red



Ia, Y = H; X = H	m.p. 109-10°	Ie, Y = H; X = m-Cl	m.p. 124-25°
b, Y = H; X = p-CH ₃	m.p. 124-25°	f, Y = p-CH ₃ ; X = H	m.p. 115-16°
c, Y = H; X = p-OCH ₃	m.p. 90-91°	g, Y = p-CH ₃ ; X = p-CH ₃	m.p. 104-05°
d, Y = H; X = p-Cl	m.p. 139-40°	h, Y = p-CH ₃ ; X = p-Cl	m.p. 135-36°

orange colour and the formation of free TNBSA. The rate of decomposition increases with the polarity of the solvent and with the electron donor power of the substituents X and Y. Gaseous BF₃ strongly accelerated the reaction. When the spontaneous decomposition is fast (1 - 6 hours), and in any case in the presence of BF₃, the products were, in almost theoretical amounts, TNBSA and a benzo[b]-thiophene derivative II (see eq. 1). With the slower reactions some side reactions, not yet studied in detail, were noticed.



However, some special effects were noted in the conversion of the adducts to 2,3-diarylbenzo[b]thiophenes. In the case of adducts Ib, Ic, Id, Ig and Ih, in which X is a substituent para to the vinylmercapto group, the benzo[b]thiophenes formed possessed the substituent X in the 6-position, i.e. meta to the sulfur, instead of the 5-position as expected. On the other hand, adduct Ie (X = m-Cl) gave a mixture of 6- and 4-chloro-2,3-diphenylbenzo[b]thiophenes, with retention of the relative positions of the substituent and the sulfur atom.

The structures of the 2,3-diarylbenzo[b]thiophenes, suggested among other facts by the similarity of the u.v. spectra with that of 2-phenylbenzo[b]thio-

phene (7), were proved by independent synthesis by cyclization of 2-aryl-2-aryl mercaptoacetophenones III (8) in polyphosphoric acid. In addition, some of the benzo[b]thiophenes II were converted to 1,1,2-triarylethanes IV by reductive desulfurization with Raney nickel. In this way the position of the substituent X in compounds II was unambiguously proved by comparison of the 1,1,2-triaryl-ethanes obtained with authentic compounds prepared by independent synthesis.

On the other hand, in the presence of various nucleophiles, other reactions of the vinylsulphonate esters I were observed. With weak nucleophiles (hydrogen chloride, methanol, thiophenols) in inert solvents products of simple substitution of the TNBSA residue were obtained, whereas with strong nucleophiles, attack at the aromatic carbon of the trinitrobenzene ring occurred.

The reactions with weak nucleophiles were carried out in methylene chloride at room temperature and gave, in addition to 2,4,6-trinitrobenzenesulfonic acid (TNBSA) good yields of reaction products shown to have structure V (eq. 2).

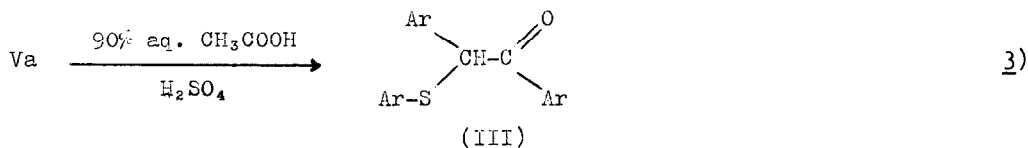


Va, Z = CH₃O-

b, Z = Ar-S-

c, Z = Cl-

In the case of the reactions with methanol, the reaction products were demonstrated to be 1,2-diaryl-2-arylmercaptomethoxyethylenes Va by their NMR spectra (which showed a sharp singlet at about 6.7 τ for the methoxy group) and by acid hydrolysis to 2-aryl-2-arylmercaptoacetophenones III (eq. 3).

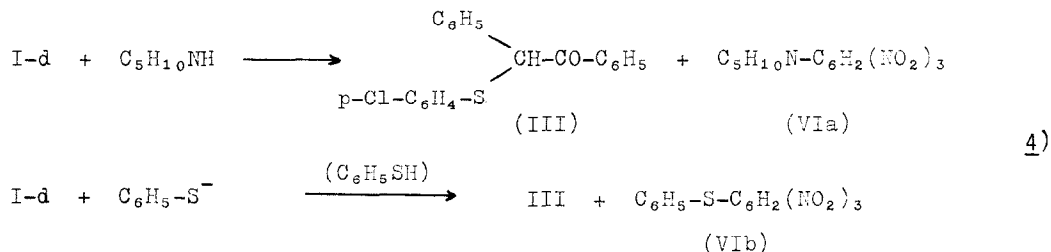


In the case of the reactions of compounds I with thiophenol the 1,2-diaryl-1,2-diarylmercaptoethylenes Vb were in some cases compared with authentic samples prepared by an independent path (10).

The 1,2-diaryl-2-arylmercaptochloroethylenes Vc, obtained by reaction of compounds I with anhydrous hydrogen chloride, were all identified by comparison with authentic samples prepared by addition of the appropriate arylsulfenyl chlo

ride to toluene and 4,4'-dimethyltoluene (2).

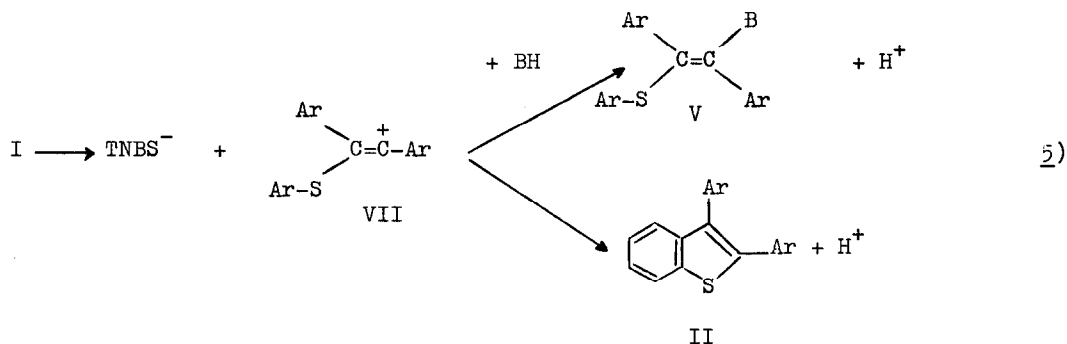
The reaction of the vinylsulphonic esters I with strong nucleophiles such as piperidine or thiophenoxide ion has so far been studied only in a preliminary manner. However it is clear that the course of the reaction is quite different from that involved in the case of weak nucleophiles. In fact, among the reaction products significant amounts of acetophenones III and 2,4,6-trinitrophenylpiperidine VIa (11) and 2,4,6-trinitrodiphenylsulfide VIb (12) (eq. 4) respectively have been isolated, suggesting attack of the nucleophile at the strongly electrophilic aromatic carbon (13). No simple substitution products such as V, have been detected.



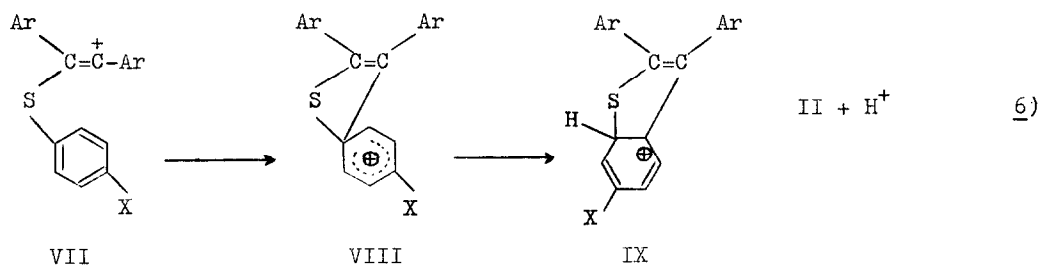
The easy cyclization of vinyl-sulphonic esters I to benzo[b]thiophene II, the strong electrophilic catalysis and the accelerating effect of electron donor substituents, as well as the nature of the reactions with weak and strong nucleophiles all suggest that the vinyl-sulphonic esters may spontaneously generate the corresponding vinyl carbonium ion VII by heterolysis of the vinyl-TNES bond. The ease with which this ionization occurs is presumably due to the presence of an excellent leaving group and the high degree of resonance stabilization of the resulting cation by the adjacent aryl groups (13). An additional factor favouring heterolysis might well be neighbouring group participation by the sulphur atom of the aryl mercapto residue (14).

Cation VII, represented for simplicity as a vinyl-carbonium ion (15), may either be captured by a nucleophile, if present, yielding V, or undergo an internal reaction leading to benzo[b]thiophene derivatives II.

The above hypothesis is supported by the finding that when the nucleophile is strong enough to interact with I directly, the reaction follows a different course. Furthermore preliminary kinetic studies confirm the unimolecular character of the reaction and the absence of significant kinetic effects when weak nucleophiles are present (16).



The cyclization to give benzo[b]thiophenes II could represent an ordinary electrophilic attack of the vinyl cation at either of the ortho positions, with respect to the sulphur atom, of the arylmercapto residue (as in the case of the cyclization of Ie) but the rearrangement observed in most of the cases suggests the occurrence of more complex processes. It seems probable that the rearranged products arise through the initial formation of a thiacyclobutene cation VIII followed by a 1,2-sulfur shift to give IX which then suffers loss of a proton.



X = CH₃, OCH₃, Cl

We are grateful to the Consiglio Nazionale delle Ricerche, Rome, for financial support of this work.

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13. However we cannot exclude a more complex reaction scheme involving attack at sulphonyl sulfur, as well as the occurrence of other side reactions.
14. The participation by sulfur, which might lead to a thiocyclopropenium cation as intermediate, is under current investigation.
15. The geometry of the vinyl-carbonium ion as well as the stereochemistry of its reactions are under current investigation and will be discussed elsewhere.
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