Tetrahedron. Vol. 24, pp. 663 to 674. Pergamon Press 1968. Printed in Great Britain

NUCLEOPHILIC REACTIONS IN ETHYLENIC DERIVATIVES—X*

REACTIONS OF NITROBROMOSTYRENES WITH METHOXIDE AND THIOPHENOXIDE IONS

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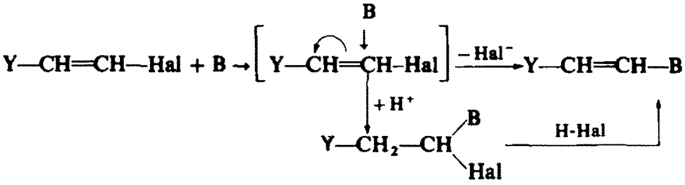
(*Received in the UK* 25 *April* 1967; *accepted for publication* 17 *May* 1967)

Abstract—The reactions of *cis* and *trans* *p*-nitro-β-bromostyrene and 2-4-dinitro-β-bromostyrene with methoxide and thiophenoxide ions in methanol have been studied and their rates measured. Whereas the thiophenoxide ion reacts by direct substitution with both *cis* and *trans* isomers, yielding the corresponding phenylmercaptoethylenes with retention of configuration, the methoxide ion yields with *cis* isomers *p*-nitro and 2-4-dinitrophenylacetylenes and with the *trans* isomers dimethoxy-derivatives [1-1-dimethoxy-2-*p*-nitro (respectively 2,4-dinitro) phenylethanes].

Isotopic experiments strongly suggest the latter reaction to be a direct substitution followed by methanol addition to the preformed vinyl ethers.

Nucleophilic reactions of activated ethylenic halides are the object of increasing interest and it has already been shown that a number of reaction paths are possible with the various substrates and nucleophiles.[1-9]

The "direct substitution" (Scheme 1), which sometimes may merge in an "addition-elimination" mechanism, seems to be the preferred path in the reaction of activated substrates with polarizable non strongly basic nucleophiles.[1-7,9]



(1)

Y = electron-withdrawing group.

The β-elimination (Scheme 2), which may or may not be followed by addition, competes favourably with the "direct substitution" in the reaction of alkoxide ions particularly when the leaving groups are *trans* related[1,2]

$$\text{Y—CH═CH—Hal} + \text{B} \rightarrow \text{Y—C≡C—H} + \text{HB}^+ + \text{Hal}^- \rightarrow \text{Y—CH═CH—B} \qquad (2)$$

When β-elimination is not possible, competition between substitution and α-elimination, usually occurring with rearrangement (Scheme 3), has been observed in non activated systems.[7,8]

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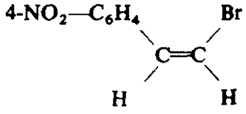
* Part IX, L. Di Nunno, G. Modena and G. Scorrano, *J. Chem. Soc.* (B) 1186 (1966).

$$R_2C{=}CH{-}Hal + B \rightarrow R{-}C{\equiv}C{-}R + Hal^- + BH^+ \qquad (3)$$

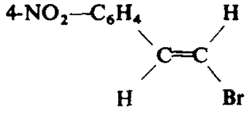
The direct substitution usually occurs with retention of configuration but cases are known in which the most thermodynamically stable isomer is the only one formed.[2,4,6]

The competition between "direct substitution" and β-elimination is one of the most interesting aspects of the nucleophilic reactivity of halogeno-ethylenes. So far it has been studied in detail only in the case of aryl sulphonyl-halogenoethylenes[10] and it seemed desirable an investigation in another system. Consequently a research was undertaken on the nucleophilic reactivity of halogeno-styrenes, in which the activating group is quite different and the activation may be graduated by suitable substitution in the phenyl ring.

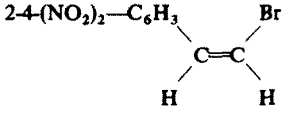
In this paper the results of the reactions of *cis* and *trans* 4-nitro- and 2-4-dinitro-β-bromostyrenes (I–IV) with methoxide and thiophenoxide ions are reported.



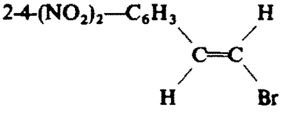
I



II



III



IV

The reactions of I and II with NaOH in ethanol and propan-2-ol were studied by Cristol *et al.*[11] mainly in respect to the elimination leading to acetylene. Miller and Yonan,[9] on the other hand, studied the halogen exchange of I and II finding evidence in favour of a direct substitution with retention of configuration.

RESULTS

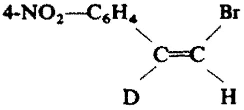
Substrates and products of reactions

The mononitro-β-bromostyrenes I and II were prepared by known methods[11,12] whereas the dinitro derivatives III and IV had not been described earlier.

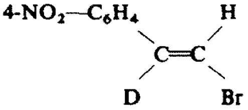
cis-2-4-Dinitro-β-bromostyrene III was prepared by decarboxylative dehalogenation of *erythro*-α-β-dibromo-β-(2-4-dinitrophenyl) propionic acid in acetone following the known procedure for the preparation of I.[11]

The *trans* isomer IV was obtained by thermal isomerization of III or in better yields by bromination of III and debromination of the resulting tribromide with iodide ion (Experimental). This sequence of reactions has been checked by the *cis*-*trans* conversion of the mono-nitro derivative I into II which occurred in a quantitative yield. The assignment of configuration is also in agreement with the IR spectra of compounds III and IV as well as with other chemical evidence (see later).

The *trans* α-deutero-β-bromonitrostyrene IIa was prepared by addition of DBr to *p*-nitrophenyl-acetylene V. The *cis* deutero-bromonitrostyrene Ia was obtained by UV isomerization of IIa.



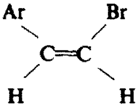
Ia



IIa

Products of reactions with CH_3O^-

cis-β-Bromostyrenes I and III yield the corresponding *p*-nitrophenylacetylene V and 2-4-dinitrophenylacetylene VI, as previously reported[13] (Equ. 4). The rate of the base catalyzed addition of methanol to the acetylene is slow enough in the conditions used and it does not interfere with the simple elimination reaction, as it was found in the case of *cis* aryl sulphonyl-halogeno-ethylenes.[2, 10] *trans*-β-Bromostyrenes II and IV yield the 1-1-dimethoxy-2-nitrophenylethanes VII and VIII.*

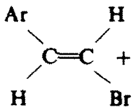


$$+ CH_3O^- \rightarrow Ar—C\equiv CH + CH_3OH + Br^- \qquad (4)$$

I, III V, VI

I, V : $Ar = 4\text{-}NO_2—C_6H_4$
III, VI : $Ar = 2\text{-}4\text{-}(NO_2)_2—C_6H_3$

Since the reactions of *trans* β-bromostyrenes II and IV with methoxide ion are much slower than those of the *cis* isomers (see below), VII and VIII could result from a subsequent addition of methanol, catalyzed by methoxide ion, to acetylenes V and VI initially formed by dehydrohalogenation of II and IV. However it was proved that this is not the case,† since the deuterobromostyrene II yields, with similar experimental conditions, a dimethoxy derivative which still contains almost all (75%) the deuterium present in the starting material.



$$+ CH_3O^- \xrightarrow{CH_3OH} Ar—CH_2—CH(OCH_3)_2 + Br^- \qquad (5)$$

II, IV VII, VIII

II, VII : $Ar = 4\text{-}NO_2—C_6H_4$
IV, VIII : $Ar = 2\text{-}4\text{-}(NO_2)_2—C_6H_3$

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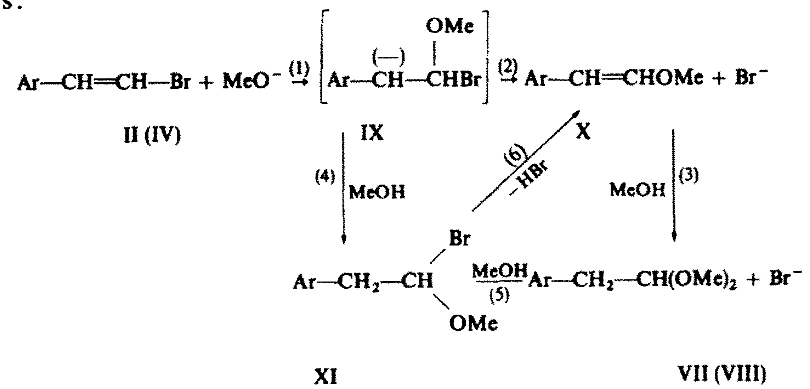
[*] Similar results have been obtained in the reaction of II with NaOH in ethanol by Cristol and coworkers[11b] who advanced some hypotheses on the mechanism of the reaction similar to those discussed in this paper.

[†] This test was run with the mononitro-derivative but the conclusions should be valid also for the dinitroderivative.

Moreover no hydrogen deuterium isotope effect was detected (see below) at variance with what was found in the case of the *cis* isomer.[‡]

The small decrease in deuterium content suggests that the elimination-addition path is partially responsible for the formation of VII. However, it was independently observed that the dimethoxy derivative VII exchanges the methylenic hydrogens fairly fast when treated with methoxide ion in methanol. It seems therefore more probable that the partial exchange observed is an artefact and that it is not directly related to the true reaction.

The routes of formation of VII (or VIII) from II (or IV) may be formulated as follows:



The attack of the nucleophile on the β carbon (reaction 1) yields the carbanion IX and by loss of bromide ion (reaction 2) the vinyl ether X (if the bond making is concerted with the bond breaking process, IX is the transition state toward the formation of X). Subsequently X adds a molecule of solvent (reaction 3) forming the acetal VII (VIII in the case of the dinitro derivative).

Alternatively the carbanion IX may capture a proton from the solvent (reaction 4) yielding the α-bromo ether XI which should easily give VII (or VIII) by solvolysis (reaction 5). An elimination addition pathway may be also envisaged (reactions 6, 3) for the formation of the observed final products.

Even if the vinyl ether X was not detected either as final product or as transient species, we think it probable that the reactions follow the route (1)–(2)–(3), i.e. the methoxide ion directly displaces the halide ion and the vinyl ether is rapidly consumed by reaction 3. Indeed this mechanism has been observed in the alkoxide reaction with other activated halogeno-ethylenes,[2, 3, 6, 15] and it is in line with the "direct substitution" mechanism of the reaction of thiophenoxide ion with the present substrates (see below).

Of course the other alternatives mentioned can not be ruled out and further work is needed to elucidate the details of the mechanism. However the important point of the preferential attack on β carbon by the methoxide ion seems to be proved.

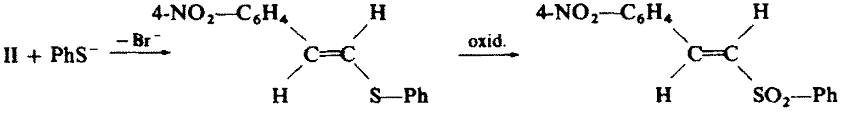
Products of reactions with thiophenoxide ion

The reactions of *trans* bromostyrenes II and IV with thiophenoxide ion yield the corresponding *trans* 4-nitro- and 2-4-dinitrostyryl phenyl sulphides XII and XIII.

[‡] Indeed the reaction of *trans* bromonitrostyrene II with potassium t-butoxide in t-butanol yields complete elimination and it does present a small but significant isotope effect ($k_H/k_D \simeq 1{\cdot}7$).[14]

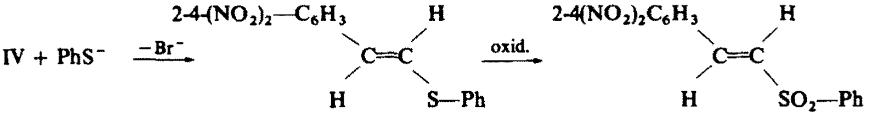
They may be oxidized to the sulphones XIV and XV by standard methods (Equs 6, 7).

The reactions of *cis* bromostyrenes I and III with thiophenoxide ion, on the other hand, yield the *cis* 4-nitrostyryl phenyl sulphide XVI (Equ. 8) and *cis* 2-4-dinitrostyryl phenyl sulphide XVII (Equ. 9) contaminated by variable amounts of the *trans* isomers XII and XIII.



XII XIV

(6)

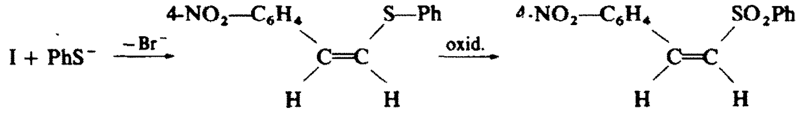


XIII XV

(7)

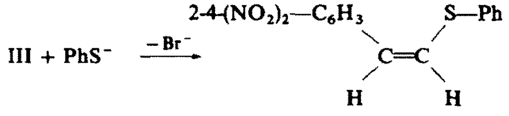
Compound XVI is easily oxidized to the corresponding sulphone XVIII.* The sulphone XVIII is thermally unstable and it is isomerized to XIV. Moreover the sulphides XVI and XVII are isomerized to sulphides XII and XIII by thiophenoxide ion.[17]

The IR spectra of XII, XIII, XIV, XV show the characteristic absorption of *trans* disubstituted ethylenes at 920–980 cm^{-1},[16] which is absent in XVI, XVII, XVIII.



XVI XVIII

(8)



XVII

(9)

It seems therefore justified to assign the *trans* configuration to sulphides XII, XIII and to the corresponding sulphones XIV and XV and the *cis* configuration to the isomers XVI, XVII, XVIII.

The reactions of *cis* bromostyrenes I and III with PhS$^-$, as above mentioned, yield a mixture of *cis* and *trans* styryl sulphides; however, the percentage of the *trans* isomer changes with the reaction conditions, with the reaction time and, in particular, with the ratio thiophenoxide ion/bromostyrene.

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* The oxidation of the dinitrostyryl phenyl sulphide XVII yields a mixture of two sulphones which rapidly converts to the pure *trans* sulphone XV.

Following the progress of the reactions by TLC it was possible to show that essentially only the *cis* isomers are present at the early stages of the reaction, but soon after *trans* isomers appear and their concentration increases with time. Moreover independent experiments, as already said, proved that *cis* styryl sulphides XVI and XVII are isomerized to the *trans* isomers by thiophenoxide ion at a rate comparable with that of formation.

It follows that the formation of a mixture of *cis* and *trans* isomers in the reactions of *cis* β-bromostyrenes with thiophenoxide ion should not be due to a lack of stereospecificity in the substitution but to a post-isomerization.

Kinetic results

The rate of the reactions of bromostyrene I–IV with methoxide and thiophenoxide ions in methanol were measured at various temperatures. They always follow second order kinetic equation and the rate coefficients (average of two or more runs usually at different initial concentrations) together with the derived Arrhenius parameters are reported on Tables 1 and 2. The rate of the reactions of the α-deutero-β-bromostyrenes Ia, IIa with methoxide ion were also measured at one temperature (see Table) and the ratio k_H/k_D evaluated. The *cis* isomer showed a kinetic isotope effect k_H/k_D equal to 2·2[13] which was absent in the *trans* isomer.

DISCUSSION

The reactions of 4-nitro- and 2-4-dinitro-β-bromostyrenes have general features similar to those observed in other nucleophilic reactions of activated ethylenic halides. With thiophenoxide ion the reactions undoubtedly follow a mechanism of direct substitution as proved by the stereochemical course (retention of configuration) and by the fairly similar rate of reaction of *cis* and *trans* isomers which depends on similar values of energies and entropies of activation. As expected the dinitro derivatives are more reactive than the mononitro and the increase in rate of reaction is essentially due to a lower activation energy.

With the styrene substrate therefore the preferential attack of the "soft"[18] nucleophile to the ethylenic carbon is once again found as well as it is the mechanism of direct substitution with its characteristic stereochemistry, which we have discussed in other instances.[2]

With methoxide ion the configuration of the substrates determines the mechanism of the reactions. *cis*-Bromostyrenes react by elimination because of the favourable steric arrangement of the hydrogen *trans* to the halogen. On the other hand the *trans* isomers, where only a *cis* elimination could be possible, react by direct substitution. This seems to be true even if the substitution is complicated by subsequent reactions which made impossible the analysis of the stereochemistry.

The kinetic results of the methoxide reaction lead by themselves to the same conclusion since it is well known[1, 3, 10] that the rates of direct substitution are not strongly effected by the configuration of the substrates whereas in the present case very large differences in rate are found between *cis* and *trans* isomers. The possibility that the *trans* isomers also react by elimination followed by addition to the phenylacetylene is ruled out by the almost complete preservation of deuterium in the reaction product of the *trans* *p*-nitro-α-deutero-bromostyrene.

TABLE 1. RATE COEFFICIENTS AND QUANTITIES OF ACTIVATION FOR THE REACTIONS OF BROMOSTYRENES I–IV ($0{\cdot}3$–$1{\cdot}5 \times 10^{-2}$M) WITH METHOXIDE ION ($0{\cdot}2$–10×10^{-2}M) IN METHANOL

		Temperature							Ea	ΔS_{25°
		0°	13°	25°	40°	60°	78·25°	100°	(Kcal/mole)	(e.u.)
cis $4\text{-}NO_2—C_6H_4—CH{=}CH—Br$	$k \times 10^3$ (mole^{-1} l. sec^{-1})	—	0·12	0·71[a]	5·38	—		—	25·0[a]	+8·8
cis $4\text{-}NO_2—C_6H_4—CD{=}CH—Br$		—	—	0·32[a]	—	—	—		—	—
trans $4\text{-}NO_2—C_6H_4—CH{=}CH—Br$		—	—	0·0016[b]	—	0·145	0·97	7·98	25·1	−2·8
trans $4\text{-}NO_2—C_6H_4—CD{=}CH—Br$		—	—	—	—	—	0·98	—	—	—
cis $2\text{-}4\text{-}(NO_2)_2—C_6H_3—CH{=}CH—Br$		49	265	1070	—	—	—	—	19·9	+6·3
trans $2\text{-}4\text{-}(NO_2)_2—C_6H_3—CH{=}CH—Br$		0·389	1·76	7·20	—	—	—	—	18·9	−7·1

[a] Data taken from Ref. 13.

[b] Extrapolated from the data at higher temps.

TABLE 2. RATE COEFFICIENTS AND QUANTITIES OF ACTIVATION FOR THE REACTIONS OF BROMOSTYRENES ($0{\cdot}34$–$1{\cdot}4 \times 10^{-2}$M) WITH THIOPHENOXIDE ION ($0{\cdot}48$–6×10^{-2}M) IN METHANOL

		Temperature						Ea	ΔS_{25°
		−20°	−10°	0°	13°	25°	40°	(Kcal/mole)	(e.u.)
cis $4\text{-}NO_2—C_6H_4—CH{=}CH—Br$	$k \times 10^3$ (mole^{-1} l. sec^{-1})	—	—	—	0·18	0·69	2·97	18·9	−11·6
cis $4\text{-}NO_2—C_6H_4—CD{=}CH—Br$		—	—	—	—	0·72	—	—	—
trans $4\text{-}NO_2—C_6H_4—CH{=}CH—Br$		—	—	—	0·55	2·20	9·24	18·2	−11·6
cis $2\text{-}4\text{-}(NO_2)_2—C_6H_3—CH{=}CH—Br$		—	—	115	357	1020	—	13·8	−14·3
trans $2\text{-}4\text{-}(NO_2)_2—C_6H_3—CH{=}CH—Br$		834	2020	5230	—	35,300[a]	—	12·4	−11·8

[a] Extrapolated from the data at lower temps.

It is interesting to note at this point, even if the problem will be discussed elsewhere,* that the elimination in the *cis* bromostyrene has not the usual features of the elimination leading to acetylenes[19] since it has a positive isotope effect which supports the rate determining character of the C—H bond breaking.

Another aspect to be briefly discussed is the diversity of the ratios k_{trans}/k_{cis} of the reactions of mononitro and dinitro-β-bromostyrenes with thiophenoxide ion. The mono-nitrostyrenes present a ratio of about 3, which is quite normal for ethylenic substitution reactions even if the *cis* isomer is often the faster,[2,3] whereas the dinitro have a ratio of about 50 at 0°.

This abnormal value probably depends more on a decreased reactivity of the *cis* isomer than on an increased reactivity of the *trans* Molecular models show that steric interactions between the *ortho* nitro group and the bromine are possible in the *cis* isomer and they may force the phenyl ring out of the plane of the double bond, thus decreasing the electron-withdrawing power of it.

EXPERIMENTAL†

The IR spectra were recorded with a Beckman IR 8 instrument and the NMR spectra with a Varian DP-60 spectrometer.

Materials

cis p-*Nitro-β-bromostyrene* I (m.p. 50–51°, from pet. ether 80–120°) was prepared by treatment of *trans* *p*-nitrocinnamic acid dibromide with $NaHCO_3$ in dry acetone following the general procedure of Cristol and Norris.[11]

trans p-*Nitro-β-bromostyrene* II was prepared by iodine catalysed isomerization of I at 120–140° under N_2 for about 15 hr. The product was then easily purified by crystallization from MeOH (m.p. 159–160°[11,12]). It was also prepared by bromination of I followed by debromination with NaI as described below for the dinitro derivative IV, method B.

cis 2-4-*Dinitro-β-bromostyrene* III. The procedure used in the case of the mononitro derivative was followed: *trans* 2-4-dinitrocinnamic acid[20] (23·8 g, 0·1 mole) was brominated by adding bromine (26 g, 0·16 mole) dropwise and heating on a steam bath for 12 hr with stirring. By cooling some 2-4-dinitrocinnamic acid dibromide crystallized and the precipitation was completed by dilution with water (yield 24 g, m.p. 210–212°).[21] *trans* 2-4-Dinitrocinnamic acid dibromide (20 g, 0·05 mole) was dissolved in 350 ml acetone and $NaHCO_3$ (14·2 g, 0·17 mole) was added. The reaction mixture was refluxed for 20 hr; then the mineral salt was removed by filtration, the solvent evaporated and the crude material washed with a 2% $NaHCO_3$aq. After crystallization from pet. ether (80–120°) the compound melted at 80–81°. (Found: C, 34·57; H, 1·84; Br, 28·97; N, 10·11. $C_8H_5BrN_2O_4$ requires: C, 35·11; H, 1·85; Br, 29·27; N, 10·26%.)

trans 2-4-*Dinitro-β-bromostyrene*

Method A. cis 2-4-dinitro-β-bromostyrene was isomerized to the corresponding *trans* isomer by heating at 150° for 8 hr under N_2, in the presence of traces of I_2. The conversion was not quantitative but pure *trans* 2-4-dinitro-β-bromostyrene was easily obtained by crystallization of the mixture from MeOH (m.p. 97–98°).

Method B. cis 2-4-dinitro-β-bromostyrene (0·020 mole, 5·5 g) was brominated in AcOH at the steam-bath temp with Br_2 in slight excess (3·5 g, 0·022 mole) for 9 hr. A brown reddish oil was then separated by dilution with water and extracted with ether. The ethereal soln was washed with $NaHCO_3$aq, $NaHSO_3$aq and, after drying over Na_2SO_4, freed from the solvent. The oily residue was directly dissolved in a soln of NaI (12 g, 0·08 mole) in aqueous MeOH (1/4, 150 ml) and refluxed for several hr. Most of the alcohol was then distilled off, and the product precipitated by addition of water and the I_2 reduced with $Na_2S_2O_3$. The product was filtered off and thoroughly washed with a dil $Na_2S_2O_3$aq and water. The crude material (4·7 g) was crystallized from MeOH (m.p. 97–98°). (Found: C, 34·35; H, 1·84; Br, 29·18; N, 9·99. $C_8H_5BrN_2O_4$ requires: C, 35·11; H, 1·85; Br, 29·27; N, 10·26%.)

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* For a preliminary report see Ref. 13.

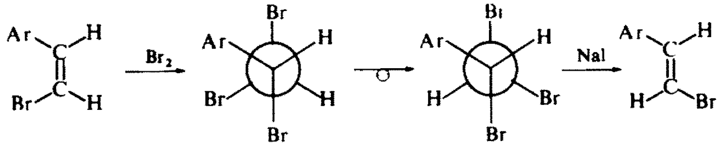
† M.p.s are uncorrected.

Configurations of cis *and* trans *2-4-dinitro-β-bromostyrenes*

The *cis* configuration was assigned to the product, m.p. 80–81°, and the *trans* configuration to the one m.p. 97–98° on the following bases:

(i) The known stereospecificity[11, 12] of the decarboxylative debromination used for the preparation of the isomer, m.p. 80–81°.
(ii) The thermal isomerization of the lower to the higher melting product.
(iii) The different reactivity of the two isomers with methoxide ion. In agreement with the configurations proposed, the lower melting product (*cis* isomer) reacts faster and yields the dinitrophenylacetylene as well it does the mono-nitrostyrene of known configuration.
(iv) The IR spectrum of the isomer with m.p. 97–98° has an absorption band of high intensity at 930 cm^{-1}, characteristic of *trans* disubstituted ethylenes,[16] which is not present in the lower melting isomer (similar spectral features are observed in the mononitro derivatives).

The configurations proposed are also in agreement with the sequence of bromination and debromination through which the *trans* isomer was prepared (method B). In fact, as may be seen from the Newman projections, the *trans* elimination of bromine from the tribromide XIX should yield the *trans* isomer independently from the configuration of the starting material as the conformation XIXb should be preferred over XIXa.[22]



III (I) XIXa XIXb IV (II)

The procedure was also tested with the mono-nitrostyrene of known configuration and the same result was obtained.

trans *4-Nitro-α-deutero-β-bromostyrene.* Deuterium bromide was added to 4-nitrophenylacetylene in chloroform following a procedure reported[23] for the addition of HBr. However, in our experience the reaction even after 4–5 days is not complete. After evaporation of the solvent the crude material was purified by several crystallizations from MeOH (m.p. 159–160°, mixed m.p. with the light compound not depressed).

The IR spectrum of the deuterated *trans* bromonitrostyrene presented a number of modifications in the region 670–940 cm^{-1}. Taking as base the absorption at 682 cm^{-1} present in the light compound but not in the deuterated one the deuterium was estimated to be about 0·7 atom per molecule.

The NMR analysis confirmed these results. The *trans* 4-nitro-β-bromostyrene gives for the ethylenic hydrogens a single line at 2·61 τ; the *cis* isomer obtained by UV isomerization of the *trans*[13] shows an AB quartet for the ethylenic hydrogens (τ_α 2·85, τ_β 3·34; $J_{\alpha-\beta}$ 8·2 c/s). The NMR spectra of the deuterated compounds show a decrease in the intensity of the single line at 2·61 τ in the *trans* isomer and only in the doublet at 2·85 in the *cis*. Using as internal standard the multiplet of the aromatic protons a content of 0·73 atom of deuterium per molecule could be calculated.

Products of the reactions of cis *and* trans *nitro-β-bromostyrenes* I–IV *with methoxide ion in methanol*

The title compounds (0·01 mole) were reacted with methoxide ion in MeOH under conditions similar to those used in the kinetic experiments. At completion of the reaction the solvent was evaporated and the residue diluted with water. The reaction product, always in high yield, was filtered off or, when liquid, extracted with ether.

cis-*4-Nitro-β-bromostyrene* I yielded *p*-nitrophenylacetylene V, m.p. 150 (lit.[11] 147–149°).

cis-*2-4-Dinitro-β-bromostyrene* III yielded similarly VI (m.p. 94·5–95·5°, from EtOH), The structure was proved by elemental analysis, qualitative tests and the IR spectrum which presents the characteristic absorption of ≡C—H stretching at 3325 cm^{-1}.[16a] (Found: C, 50·9; H, 2·17; N, 14·64. $C_8H_4N_2O_4$ requires: C, 50·01; H, 2·09; N, 14·59%.)

trans *4-Nitro-β-bromostyrene* II yielded VII, b.p. 124–125°/1 mm. (Found: C, 57·00; H, 6·32; N, 6·87. $C_{10}H_{13}NO_4$ requires: C, 56·85; H, 5·95; N, 6·63%); NMR spectrum in CCl_4: 7·06 (doublet, CH_2), 6·49 (singlet, OMe) 5·45 τ (triplet, CH) and the multiplet characteristic of aromatic hydrogens. Compound VII yields the expected oxime m.p. 154–155°[24] by treatment with hydroxylamine hydrochloride, after hydrolysis with HCl.

trans 2-4-*Dinitro-β-bromostyrene* IV yielded VIII m.p. 49–50° from aqueous EtOH. (Found: C, 46·28; H, 4·60; N, 11·20; $C_{10}H_{12}N_2O_6$ requires: C, 46·88; H, 4·72; N, 10·94%); NMR spectrum in CCl_4: 6·68 (doublet, CH_2); 6·65 (singlet, OMe); 5·45 τ (triplet, CH) which, with hydroxylamine hydrochloride in the conditions above indicated, yielded the corresponding oxime: m.p. 117–118°, from EtOH. (Found: C, 43·11; H, 3·39; N, 18·59. $C_8H_7N_3O_5$ requires: C, 42·68; H, 3·13; N, 18·6%.)

Reaction of trans *4-nitrophenyl-α-deutero-β-bromostyrene with methoxide ion*

The reaction was run as reported for the light compound. The oily product was transformed into the oxime and the deuterium content evaluated by NMR spectroscopy [6·14 (doublet, CH_2), 3·13 (triplet, CH), −0·59 τ (singlet, =N—OH) and the multiplet of aromatic hydrogens]. The analysis gives a deuterium content of 0·54 atom per molecule at the CH_2. The deuterated bromostyrene had a deuterium content of 0·73 atom per molecule.

*Hydrogen/deuterium exchange in 1-1-dimethoxy 2(*p*-nitrophenyl) ethane*

The title compound (1·00 g, 0·005 mole) was dissolved in 30 ml of 0·03M MeONa in MeOD and the soln boiled for 40 hr.[*] The 1-1-dimethoxy-2-(*p*-nitrophenyl) ethane was then recovered and distilled at reduced press. The NMR spectrum showed that exchange H/D had occurred at a large extent (≃75%).

Products of reactions of cis *and* trans *4-nitro-β-bromostyrene with thiophenoxide ion in methanol*

The title compounds (0·001 mole) were reacted in conditions similar to those used in the kinetic experiments with thiophenoxide ion in MeOH. At completion, the soln was diluted with water, the crude material filtered off and purified as described below. The yields were generally quantitative.

trans 4-*Nitro-β-bromostyrene* II yielded *trans* 4-nitrostyryl phenyl sulphide XII, m.p. 73–74°[11] from EtOH. IR spectrum (CCl_4): band at 935 cm^{-1} (*trans* disubstituted ethylene).

trans 4-*Nitrostyryl sulphide* XII by oxidation with peracetic acid in AcOH yielded the corresponding sulphone XIV (from EtOH) m.p. 176–177°[†] (lit.: 158–160°[25]; 169–170°[26]). (Found: C, 58·18; H, 3·84; N, 4·7; S, 13·63. $C_{14}H_{11}NO_4S$ requires: C, 58·12; H, 3·83; N, 4·84; S, 14·06%.)

trans 2-4-*Dinitro-β-bromostyrene* IV yielded *trans* XIII, m.p. 114–115° (from EtOH). IR spectrum (CCl_4): band at 933 cm^{-1} (*trans* disubstituted ethylene). (Found: C, 55·04; H, 3·31; N, 8·90; S, 10·58. $C_{14}H_{10}N_2O_4S$ requires: C, 55·62; H, 3·33; N, 9·26; S, 10·61%.)

The sulphone XV obtained by oxidation with peracetic acid of the above reported sulphide melts at 148–149° (from EtOH).[‡] (Found: C, 50·43; H, 3·26; N, 8·39; S, 11·4. $C_{14}H_{10}N_2O_6S$ requires: C, 50·30; H, 3·01; N, 8·38; S, 11·74%.)

cis 4-*Nitro-β-bromostyrene* I yielded a crude material, m.p. 90–95° which by crystallization from EtOH gave pure *cis* 4-nitrostyryl phenyl sulphide XVI, m.p. 104–105°. (Found: C, 65·22; H, 4·23; N, 5·65; S, 12·20. $C_{14}H_{11}NO_2S$ requires: C, 65·34; H, 3·91; N, 5·44; S, 12·46%.)

From the mother liquors some *trans* XII was recovered. The amount changed with the experimental conditions and when thiophenoxide ion concentration did not largely exceed bromostyrene, it was in the range of 5–15%.

cis 4-*Nitrostyryl phenyl sulphide* XVI yielded by oxidation with peracetic acid in AcOH the corresponding sulphone XVIII, m.p. 107–108° from EtOH. (Found: C, 58·29; H, 3·89; N, 4·89; S, 13·7. $C_{14}H_{11}NO_4S$ requires: C, 58·12; H, 3·83; N, 4·84; S, 14·06%.)

cis 4-*Nitrostyryl phenyl sulphone* XVIII yielded quantitatively the *trans* isomer XIV when heated under N_2 at 160° for 8 hr in presence of traces of I_2.

cis 2-4-*Dinitro-β-bromostyrene* III yielded a mixture of *cis* and *trans* phenylmercaptodinitrostyrenes

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[*] The half-life of the reaction of *trans* *p*-nitro-β-bromostyrene II with methoxide ion, at comparable initial concentrations of the reagents, is about 9 hours at 60°.

[†] The IR spectrum of the sulphone XIV, taken in $CHCl_3$, showed two absorption bands in the region 960–980 cm^{-1} (at 962 and 980 cm^{-1}, respectively). Both bands were absent in the *cis* isomer.

[‡] The IR spectrum of the sulphone XV taken in $CHCl_3$ showed two absorption bands in the region 900–970 cm^{-1} (at 920 and 963 cm^{-1}, respectively).

in variable proportion depending on reaction time and on the ratio thiophenoxide/styrene. When almost equimolar concentrations of thiophenoxide ion and styrene were used *cis*/*trans* ratios near to 1 were found but even 100% *trans* was sometimes formed when excess of thiophenoxide ion and/or longer reactions time were used. The *cis* isomer XVII was isolated from the reacting soln by cooling it before completion (2–3 half-lives). After crystallization from EtOH it melted at 101–102. (Found: C, 55·18; H, 3·31; N, 9·18; S, 10·61. $C_{14}H_{10}N_2O_4S$ requires: C, 55·62; H, 3·33; N, 9·26; S, 10·6%.)

The sulphide XVII when oxidized with peracetic acid or with peroxibenzoic acid in chloroform yielded a mixture of *cis* and *trans* sulphones which rapidly was converted to the pure *trans* isomer XV by simply heating in a solvent or exposure to light even in the solid state. Therefore the *cis* dinitro-sulphone was not characterized.

TLC of mixture of cis *and* trans *nitrostyryl phenyl sulphides and analysis of the reaction solutions*

TLC on silica gel (HF_{254} according to Sthal) developed with hexane/pet. ether 40–70°/AcOEt (5:2·5:1) for the mono-nitrostyrenes and on silica gel (G according to Sthal) developed with pet. ether 80–120°/benzene 1:1, for the dinitrostyrenes, gave good separation of the mixture of *cis* and *trans* sulphides. Experiments with mixtures of known composition showed that the method was reliable for resolving mixtures in which one of the components was present in concentration as low as 1%. The method was used to control the purity of the compounds described and also the progress of the reactions of *cis* bromostyrenes with thiophenoxide ion.

cis 4-Nitro-β-bromostyrene was reacted with thiophenoxide ion in methanol in conditions similar to those used in the kinetic experiments. Aliquots were withdrawn at intervals and either directly analysed by TLC or, if necessary, concentrated after quenching the reaction by neutralization. Care was taken in order that the amount of the sulphide submitted to the analysis was roughly the same as that used in the check experiments with mixtures of known composition. In conversions of the order of 1–5% the concentration of the *trans* isomer was so small that it was hard to detect whereas at higher conversion times the *trans* isomer appeared in increasing proportion.

An exact evaluation of the percentage of the *trans* isomer at the early stages of the reaction is difficult with the technique used, although it was safe to consider that the *trans* isomer did not exceed 3–5%.

The reaction of *cis* 2-4-dinitro-β-bromostyrene with thiophenoxide ion was followed with the same procedure as above. A similar trend was observed and also in this case at the early stages of the reaction the *trans* sulphide formed did not account for more than 3–5% of the reaction product. However, the increase of the *trans* to *cis* ratio was in this case much faster than in the reaction of the mono-nitrostyrene.

Isomerization of cis *nitro-β-phenylmercaptostyrenes with thiophenoxide ion*

The *cis* sulphides XVI, XVII isomerized easily in the presence of thiophenoxide ion. The rate of isomerization of the dinitro derivative was much faster than that of the mono-nitro.

In fact the mono-nitro sulphide XVI was only partially isomerized by the action of thiophenoxide ion (6×10^{-2}M) in MeOH even after 48 hr at 25°. On the other hand the dinitro derivative XVII was completely converted in 15 hr at 0°.

The relevance of the *cis* to *trans* isomerization in respect to the finding of the *trans* sulphide in the products of the reaction of *cis* bromostyrene with thiophenoxide ion was better evaluated by the experiments described below.

Considering that the kinetic experiments were run at concentration of the reagents of the order of 1×10^{-2}M, a methanolic solution of *cis* XVI ($1{\cdot}4 \times 10^{-4}$M) was reacted at 25° with thiophenoxide ion ($1{\cdot}4 \times 10^{-2}$M) for 15 min (time corresponding to 1% of reaction). Then the soln was analysed by TCL and a small but significant amount of the *trans* isomer was detected.

A similar experiment was performed at 0° with *cis* 2-4-dinitrostyryl phenyl sulphide (sulphide, $1{\cdot}3 \times 10^{-4}$M; PhS^-, $1{\cdot}4 \times 10^{-2}$M; time 25 secs, corresponding to 4% of reaction) and the analysis by TLC of the reacting soln showed that a significant *cis* → *trans* isomerization of the sulphides had occurred.

Kinetics measurements

Standard techniques, as previously reported,[2] were used, whenever possible, for the reactions of nitro-β-bromostyrenes with methoxide and thiophenoxide ions, following the progress of the reaction by argentometric titration. In the case of the thiophenoxide reaction the thiophenol was extracted with CCl_4 after acidification. MeOH was analar grade commercial product further purified by standard methods.[27] The rate of the reaction of *trans* 4-nitro-β-bromostyrene with methoxide ion was measured in the range

60–100° and therefore the sealed ampoule technique was adopted. On the other hand the reactions of *trans* 2-4-dinitro-β-bromostyrene with Ph-S$^-$ were too fast to be measured in the usual temp range. They were done in the range −20–0° and the following technique was used: the reagents solns were placed initially in separate arms of an inverted Y tube and after thermostatation were mixed rapidly by righting the tube and allowing the soln to react in one of the arms which was flask-shaped at the bottom. Quenching by rapid addition of dil HNO_3 was followed by the usual analysis.

Rate coefficients and Arrhenius parameters were calculated in the usual way[28] taking into account, when necessary, the solvent expansion and contraction.[29]

Acknowledgements—We thank Prof. F. Taddei, Istituto di Chimica Organica e di Chimica Industriale, Bologna, for the NMR spectra. This work was supported by a grant from the Consiglio Nazionale delle Ricerche, Roma.

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