Stereospecific Synthesis of *cis*- and *trans*-2-Halogenovinyl Ketones. Stereochemistry of Nucleophilic Substitutions at Vinylic Carbon

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Hydrogen and deuterium halides combine with ethynyl ketones at −40° to give predominantly *cis*-2-halogenovinyl ketones, and at 20° to give *trans*-2-halogenovinyl ketones exclusively. The halides can be converted into 2-phenylthiovinyl ketones and into 2-phenylsulphonyl ketones with retention of configuration. The *trans*-halogenovinyl ketones and the *trans*-sulphones are thermodynamically more stable than the respective *cis*-isomers; however, the *trans*-sulphides are less stable than the *cis*-sulphides. The behaviour of the sulphides is interpreted in terms of electrostatic interaction between the sulphur atom and the carbonyl oxygen.

2-HALOGENOVINYL KETONES can exist as *trans*- and *cis*-isomers, and yet the general methods of synthesis hitherto employed[1] appear to lead only to the *trans*-isomers. To the best of our knowledge the only *cis*,-*trans* pair known is that of 2-chlorovinyl methyl ketone.[2] A few other examples of geometric isomers have been reported in the case of mono- or di-substituted 2-halogenovinyl ketones $R^1CO{\cdot}CR^2{:}CR^3X$.[1]

We have found[3] that *cis*-2-chlorovinyl ketones (II) can be obtained by adding equimolecular quantities of hydrogen chloride in chloroform–diethyl ether to a solution of an ethynyl ketone (I) in chloroform at −40°. Conversion is complete in 6—24 hr. The crude product contains small quantities of the original ethynyl ketone (2—3%) and of *trans*-chlorovinyl ketone (III) (10—20%), which can be removed by crystallisation or t.l.c. The *cis*-configuration of the compounds obtained is confirmed by the absence of the strong ethylenic i.r. absorption at *ca.* 930 cm.$^{-1}$, typical of *trans*-isomers (III).

A slight excess of hydrogen chloride or a higher reaction temperature results in rapid *cis* → *trans* inversion.

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[1] (*a*) N. K. Kochetkov, *Uspekhi Khim.*, 1955, **24**, 32; (*b*) A. E. Pohland and W. R. Berson, *Chem. Rev.*, 1966, **66**, 161.

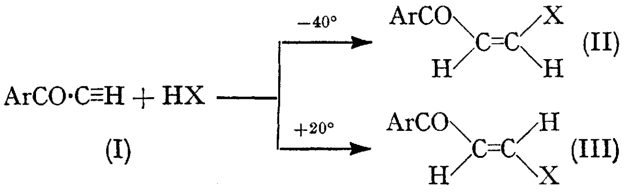
[2] A. I. Ivanov, V. G. Vinokurov, T. V. Protopopova, and A. P. Skoldinov, *Zhur. obshchei Khim.*, 1964, **34**, 354.

[3] Preliminary communications, (*a*) D. Landini and F. Montanari, *Chem. Comm.*, 1967, 180; (*b*) E. Angeletti and F. Montanari, *Boll. sci. Fac. Chim. ind. Bologna*, 1958, **16**, 140.

At 20° in the presence of hydrogen chloride (1·05 equiv.), sterically pure *trans*-isomers (III) can be obtained. Because of the high yields and ease of application the latter method compares very well with those normally used for the synthesis of *trans*-2-chlorovinyl ketones (III), namely the addition of acyl chlorides to acetylene,[1,4] and the chlorination of β-oxoacetaldehydes.[1,5] Thus the addition of hydrogen chloride to ethynyl ketones is an easy way of obtaining both geometric isomers (II) and (III) from a common intermediate.

The same conditions apply to the synthesis of *cis*- and *trans*-aryl 2-bromovinyl ketones and to the synthesis of *cis*- and *trans*-aryl 1-deuterio-2-chlorovinyl (or bromovinyl) ketones (IV) and (V) by use of deuterium chloride or bromide.

The addition of hydrogen iodide in acetic acid–chloroform at —40° yields *cis*-aryl 2-iodovinyl ketones (II; X = I) and the addition of the same acid in acetic acid at room temperature yields a mixture of *cis*-(II) and *trans*-isomers (III; X = I).



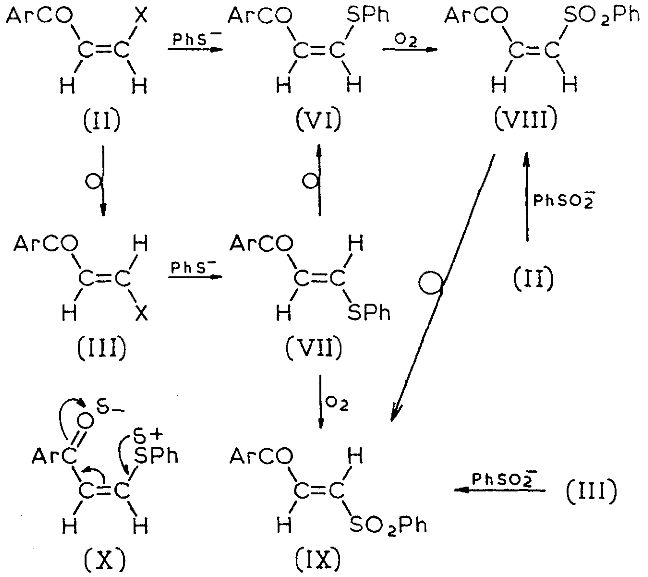
X = Cl, Br, or I

$(I) + DX \longrightarrow ArCO{\cdot}CD{=}CHX$

(IV) *cis*, (V) *trans*, X = Cl or Br

The addition of hydrogen halides to ethynyl ketones at —40° follows the normal *trans* stereochemical behaviour of heterolytic additions to triple bonds. As in other acetylenic systems bonded to electron-withdrawing groups the reaction probably proceeds *via* initial nucleophilic attack of the halide ion on the triple bond.[6]

The availability of both isomeric series of 2-halogenovinyl ketones makes possible a study of the stereochemistry of nucleophilic substitutions of halogen. In aqueous acetone at 0°, the substitution of benzenethiolate for halogen in the compounds (II) and (III) yields arylthiovinyl ketones (VI) and (VII) with retention of configuration. The *cis*-sulphides (VI) are obtained sterically pure; the *trans*-sulphides (VII) are accompanied by small quantities of *cis*-isomers. Higher temperatures or an accumulation of base in the reaction medium caused by too rapid an addition of reagent catalyses easy *trans* → *cis* isomerisation (see later). The same *cis*-arylthiovinyl ketones (VI) are obtained by base-catalysed addition of benzenethiols to ethynyl ketones (I).[7] The sulphides (VI) and (VII) are oxidised by perbenzoic acid to the corresponding sulphones (VIII) and (IX). The latter may also be obtained by nucleophilic substitution of sulphinate for halogen. The reaction occurs with retention of configuration, but in the case of the *cis*-sulphones it may be accompanied by partial *cis* → *trans* isomerisation. An analogous inversion occurs in the oxidation of the *cis*-sulphides to sulphones.



Stereochemical results and kinetic measurements[8] indicate that in halogenovinyl ketones nucleophilic substitutions with benzenethiolate ion proceeds *via* direct nucleophilic attack on the halogenated carbon. Measurements carried out[8] with 1-deuterio-2-halogenovinyl ketones (IV) and (V) have enabled us to exclude in the *cis*-series any elimination–addition mechanism, which might equally well have explained the retention of configuration observed.* These results are analogous to those normally obtained in activated ethylenic systems for nucleophilic substitutions by anionic reagents with a high nucleophilicity towards carbon.[9]

trans-2-Halogenovinyl ketones (III) and *trans*-sulphones (IX)[7b,10] are thermodynamically more stable than the respective *cis*-isomers (II) and (VIII). *trans*-Sulphides (VII), on the other hand, are much less stable than *cis*-sulphides (VI), and are converted quantitatively into the latter by base catalysis, or by heating in inert,

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* Elimination–addition is found, however, in the reactions of *cis*-2-chlorovinyl or bromovinyl ketones (II) with methoxide ion.[8]

[4] See *inter alia* (*a*) C. C. Price and J. A. Pappalardo, *J. Amer. Chem. Soc.*, 1950, **72**, 2613; (*b*) N. K. Kochetkov, A. Khorlin, and M. Karpeiskii, *Zhur. obshchei Khim.*, 1956, **26**, 595.

[5] (*a*) L. Panizzi, *Gazzetta*, 1947, **77**, 549; (*b*) A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya, *Izvest. Akad. Nauk.*, 1954, 741.

[6] (*a*) E. Winterfeldt, *Angew. Chem. Internat. Edn.*, 1967, **6**, 423; (*b*) I. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukrain. khim. Zhur.*, 1964, **30**, 1076 (*Chem. Abs.*, 1965, **62**, 5160*e*); (*c*) G. F. Dvorka and E. A. Shilov, *Kinetika i Kataliz.*, 1965, **37**, 40 (*Chem. Abs.*, 1965, **62**, 16,009*h*).

[7] (*a*) S. Ruhemann, *J. Chem. Soc.*, 1905, **87**, 461; (*b*) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 1946, 945; (*c*) W. E. Truce and R. F. Heine, *J. Amer. Chem. Soc.*, 1957, **79**, 5311.

[8] D. Landini, F. Montanari, G. Modena, and F. Naso, *J. Chem. Soc.* (*B*), 1969, 243.

[9] S. Patai and Z. Rappoport, ' The Chemistry of Alkenes,' ed. A. Patai, Interscience, London, 1964, p. 525.

[10] E. P. Kohler and R. G. Larsen, *J. Amer. Chem. Soc.*, 1935, **57**, 1448.

low-boiling solvents, such as light petroleum. The greater thermodynamic stability of *trans*-halogeno-derivatives (III) and of sulphones (IX) in comparison with the *cis*-isomers (II) and (VII) can be rationalised in terms of electrostatic and steric repulsion between the groups linked to the double bond. The greater stability of the *cis*-sulphides (VI) may be attributed to electrostatic interaction between the opposite charges stabilised on the atoms of oxygen and sulphur (X).

A short intramolecular S–O distance (2·80 Å) and molecular planarity have recently been shown[11] by crystallographic *X*-ray analysis in *cis*-mercaptovinyl ketones structurally analogous to the sulphides (VI). A similar greater stability of the *cis*-isomers has been found[12] in the case of aryl 2-halogenovinyl sulphides. The high polarisability of sulphur plays an important role in these cases.

EXPERIMENTAL

Aryl Ethynyl Ketones (I).—Chromic acid oxidation[13] of aryl ethynyl methanols[14] in aqueous acetone afforded aryl ethynyl ketones (I): *phenyl ethynyl ketone* (75%), m.p. 50—51° (from aqueous methanol) (lit.,[13] 50—51°); p-*anisyl ethynyl ketone* (92%), m.p. 87—88° (from light petroleum) (Found: C, 75·3; H, 4·8. $C_{10}H_8O_2$ requires C, 75·0; H, 5·0%); and p-*chlorophenyl ethynyl ketone* (52%), m.p. 106—107° (from light petroleum) (Found: C, 65·5; H, 3·0. C_9H_5ClO requires C, 65·7; H, 3·1%).

TABLE 1

cis- and *trans*-Aryl 2-halogenovinyl ketones *p*-$RC_6H_4{\cdot}CO{\cdot}CH{:}CHX$

R	X	Configuration	Yield[a] (%)	M.p.[b]	ν(HC:CH) (cm.⁻¹)	ν(C=O) (cm.⁻¹)	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
H	Cl	*cis*	40	4—5°		1670	C_9H_7ClO	64·8	4·2	64·7	4·2
H	Cl	*trans*	79	22—23[c]	930	1670					
OMe	Cl	*cis*	60	27—28		1670	$C_{10}H_9ClO_2$	67·3	4·6	67·1	4·6
OMe	Cl	*trans*	87	52—53[d]	927	1665					
Cl	Cl	*cis*	60	31—32		1675	$C_9H_6Cl_2O$	53·3	3·0	53·7	3·1
Cl	Cl	*trans*	85	35·5—36[e]	932	1665					
OMe	Br	*cis*	58	17—18[f]		1670	$C_{10}H_9BrO_2$	49·7	3·7	49·8	3·8
OMe	Br	*trans*	73	64—65	938	1660		49·9	3·7		
OMe	I	*cis*	63	54—55·5		1660	$C_{10}H_9IO_2$	41·9	3·0	41·7	3·1
OMe	I	*trans*	21	64—65	939	1660		42·0	3·1		

[a] After crystallisation. [b] From light petroleum–diethyl ether. [c] B.p. 99—101°/3 mm. (lit.,[1b] 92—96°/2 mm.). [d] Lit.,[1b] 47—48°. [e] Lit.,[1b] 35·5—36°. [f] n_D^{20} 1·6208.

cis-*Aryl 2-Chlorovinyl Ketones* (II).—A solution (*ca.* N) of hydrogen chloride was prepared by absorption of the dry gas in anhydrous diethyl ether, and dilution with anhydrous chloroform (3—4 vol.). This solution was standardised and an amount corresponding to 0·01 mole of HCl was added dropwise with stirring during *ca.* 90 min. to a solution of aryl ethynyl ketone (0·01 mole) in anhydrous chloroform (60 ml.) kept at −40° under nitrogen. The solution was then kept at −40° until the end of the reaction (6—24 hr.), and the solvent was then evaporated off *in vacuo* at room temperature. The residue was cis-*aryl 2-chlorovinyl ketone* (II), containing small amounts of ethynyl ketone (2—3%) and 10—20% of *trans*-isomer (III). Crystallisation from diethyl ether–light petroleum afforded sterically pure compounds (II) (40—60%; no i.r. absorption at *ca.* 930 cm.⁻¹). More quantitative separations of isomers (II) and (III) were obtained by t.l.c. [silica gel PF_{254}; n-hexane–ethyl acetate–light petroleum (2 : 1 : 1)] and fractional crystallisation. *trans*-Isomers (III) have the higher and *cis*-isomers (II) the lower R_F values. The addition of catalytic amounts of cuprous chloride, reported in the preliminary communications,[3] is not essential to the reaction.

cis-2-Chlorovinyl ketones are not very stable at room temperature, but they may be kept unaltered for many weeks at 0° in the dark. They are strongly vesicant on contact with the skin. Physical properties and analytical data are reported in Table 1.

trans-*Aryl 2-Chlorovinyl Ketones* (III).—A standard solution of hydrogen chloride in anhydrous diethyl ether–chloroform (0·0105 mole of HCl), prepared as described before, was added dropwise with stirring (30 min.) to a solution of aryl ethynyl ketone (I) (0·01 mole) in anhydrous chloroform (60 ml.) kept under nitrogen at room temperature. After 12 hr. the solution was washed with aqueous sodium hydrogen carbonate, dried and evaporated to dryness to give nearly pure *trans*-aryl 2-chlorovinyl ketones. The physical properties of the compounds are reported in Table 1.

cis-p-*Anisyl 2-Bromovinyl Ketone* (II; Ar = C_6H_4OMe-*p*, X = Br).—This was prepared like the chloro-derivative by use of a solution of hydrogen bromide in ether–chloroform. The solution was added during 3 hr. and the mixture was kept at −40° for 45 min. more. The crude product was separated from the ethynyl ketone (5—10%), and from the *trans*-isomer (15—20%) by crystallisation from light petroleum–ether (5 : 1) and by t.l.c. (see also Table 1). When longer reaction times were used the ethynyl ketone disappeared, but the percentage of the *trans*-isomer increased noticeably.

trans-p-*Anisyl 2-Bromovinyl Ketone* (III; Ar = C_6H_4OMe-*p*, X = Br).—This was prepared like the *trans*-2-chlorovinyl ketones. The crude oily product, treated with light petroleum, afforded a crystalline compound, m.p. 60—63°, containing about 5% *cis*-isomer, and was further purified by crystallisation (Table 1).

p-*Anisyl 2-Iodovinyl Ketones* (II and III, Ar = C_6H_4OMe-*p*, X = I).—(*a*) Hydrogen iodide (0·01 mole) in anhydrous

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[11] M. Mammi, D. A. Clemente, A. Del Pra, F. D'Angeli, A. C. Veronese, C. Toniolo, G. Rigatti, M. Coletta, and G. Boccalon, *Chem. Comm.*, 1968, 741.

[12] (*a*) E. Angeletti, F. Montanari, and A. Negrini, *Gazzetta*, 1957, **87**, 1086; (*b*) p. 1115.

[13] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

[14] P. Rutan and C. E. May, *J. Amer. Chem. Soc.*, 1947, **69**, 2017.

acetic acid–chloroform (1 : 3) maintained at −30° to avoid loss of iodide, was added dropwise (90 min.) under nitrogen to *p*-anisyl ethynyl ketone (0·01 mole) in anhydrous chloroform (60 ml.), kept at −40°. After 12 hr. the solution was rapidly washed with aqueous sodium hydrogen carbonate until neutral, with sodium thiosulphate, and with water. Evaporation of the solvent left cis-p-*anisyl* 2-*iodovinyl ketone*, which was separated by crystallisation (Table 1) from small amounts of ethynyl ketone (3—4%) and *trans*-isomer (10%).

(*b*) The addition of hydrogen iodide (0·0105 mole) to *p*-anisyl ethynyl ketone (0·01 mole) was carried out at room temperature (75 min.) in acetic acid solution. After 12 hr. the solution was diluted with water and extracted with chloroform, and the extracts were worked up as before to give a mixture of *cis*- and *trans*-*p*-anisyl 2-iodovinyl ketones, ethynyl ketone, and p-*anisyl* 2,2-*di-iodoethyl ketone*. Most of the latter compound (8·4%), m.p. 107—108° (from benzene–light petroleum), remained as an insoluble residue after the mixture had been treated with small amounts of diethyl ether (Found: C, 28·9; H, 2·2 $C_9H_{10}I_2O$ requires C, 28·9; H, 2·3%), τ 4·49 (t) and 5·66 (d) ($CH{\cdot}CH_2$, *J* 7·1 c./sec.) and 6·12 (s, OMe). The fraction soluble in ether was separated by t.l.c., to give trans-p-*anisyl* 2-*iodovinyl ketone* (21%; m.p. 59—63°) and the *cis*-isomer (62%; m.p. 46—49°), which were further purified by crystallisation (Table 1).

TABLE 2

cis- and *trans*-Aryl 2-phenylthiovinyl and aryl 2-phenylsulphonylvinyl ketones $p\text{-}RC_6H_4{\cdot}CO{\cdot}CH{:}CHXPh$

R	X	Congur-ation	M.p.	Crystall.[a] from	ν(C=O) (cm.⁻¹)	ν(HC:CH) (cm.⁻¹)	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
H	S	*cis*	80—81° [b]	LP	1645		$C_{15}H_{12}OS$	75·2	5·1	75·0	5·0
H	S	*trans*	76—77	EE–LP	1655	940		74·9	5·0		
OMe	S	*cis*	107—108	ET	1645		$C_{16}H_{14}O_2S$	71·4	5·2	71·1	5·2
OMe	S	*trans*	70—71	EE–LP	1650	942		71·3	5·3		
Cl	S	*cis*	125—126	LP	1655		$C_{15}H_{11}ClOS$	65·4	4·2	65·6	4·0
Cl	S	*trans*	61—62	EE–LP	1650	940		65·8	4·1		
H	SO_2	*cis*	146—147 [c]	EE–LP	1680						
H	SO_2	*trans*	113 [d]	ME	1680	955					
OMe	SO_2	*cis*	129—130	EE	1670		$C_{16}H_{14}O_4S$	63·8	4·9	63·6	4·7
OMe	SO_2	*trans*	115—116	ET	1670	955		64·0	4·9		
Cl	SO_2	*trans*	145—146	ET	1675	950	$C_{15}H_{11}ClO_4S$	59·0	3·6	58·7	3·6

[a] EE = Ethyl ether; LP = light petroleum; ET = ethanol; ME = methanol. [b] N. K. Kochetkov and V. N. Vinogradova, *Zhur. obschei Khim.*, 1957, **27**, 460, report m.p. 79·5—80·5° for the sulphide obtained from benzenethiol and *trans*-phenyl 2-chlorovinyl ketone. [c] Lit.,[10] 149°. [d] Lit.,[10] 114°.

p-*Anisyl* 1-*Deuterio*-2-*halogenovinyl Ketones* [cis-(IV) *and* trans-(V)].—*cis*- and *trans*-Chloro- and bromo-derivatives were prepared like the isotopically normal compounds, by addition of deuterium chloride (from benzoyl chloride and deuterium oxide) or deuterium bromide (from phosphorus tribromide and deuterium oxide) to *p*-anisyl ethynyl ketone. In all cases mixtures with the non-deuteriated parent acids showed no m.p. depression. The deuterium content was in the range 0·70—0·86 atoms per molecule (^1H n.m.r. analysis).

Aryl 2-*Phenylthiovinyl Ketones* [cis-(VI) *and* trans-(VII)].—(*a*) A solution of benzenethiol (1·10 g., 0·01 mole) and sodium hydroxide (0·40 g., 0·01 mole) in acetone–water (2 : 1; 30 ml.) was added dropwise with stirring during 45 min. to a solution of aryl 2-halogenovinyl ketone (0·01 mole) in the same solvent (60 ml.) kept at 0°. The cis-*aryl* 2-phenylthiovinyl ketones (VI) began to separate during the reaction, while the trans-*isomers* (VII) remained in solution. After the addition, the mixture was left at 0° for 30 min., then diluted with water, and the product was extracted with ethyl ether. The combined extracts were washed with 10% aqueous sodium hydroxide and water, dried, and evaporated to give the phenylthio-ketone (VI) or (VII) as a crystalline solid. Traces of benzenethiol were removed by washing the solid with cold light petroleum. *cis*-2-Halogenovinyl ketones (II) afforded sterically pure *cis*-aryl 2-phenylthiovinyl ketones (VI), and *trans*-2-halogenovinyl ketones (III) afforded *trans*-aryl 2-phenylthiovinyl ketones (VII), sometimes together with small amounts of *cis*-isomers (VI) (5—6%). When the reactions were carried out at higher temperatures or with a slight excess of base, the percentage of *cis*-isomers (VI) increased in the products from *trans*-2-halogenovinyl ketones (III). Under non-controlled conditions *cis*-sulphides (VI) were the only products from *trans*-isomers (III). *trans*-Sulphides (VII) were also easily isomerised to *cis*-sulphides (VI) when heated in light petroleum solutions. To avoid isomerisation, *trans*-sulphides (VII) were best crystallised by addition of light petroleum to a cooled solution of the compound in diethyl ether. Physical properties, yields, and analytical data of sulphides (VI) and (VII) are reported in Table 2.

(*b*) A solution of benzenethiol (1·10 g., 0·01 mole) and sodium hydroxide (0·48 g., 0·012 mole) in ethanol (20 ml.) was added dropwise during 15 min. at room temperature to a stirred solution of aryl ethynyl ketone (I) (0·01 mole) in the same solvent (60 ml.). *cis*-Aryl 2-phenylthiovinyl ketones (VI) began to separate during the reaction and were obtained in 80—90% yield. The crude products were nearly pure. Mixtures with the *cis*-compounds described in (*a*) showed no m.p. depression.

Aryl 2-*Phenylsulphonylvinyl Ketones* [cis-(VIII) *and* trans-(IX)].—(*a*) A solution of benzenesulphinic acid (1·42 g., 0·01 mole) and sodium hydrogen carbonate (1·26 g., 0·015 mole) in water (20 ml.) was added with stirring during 60 min. to a solution of *cis*- or *trans*-2-halogenovinyl ketone (II) or (III) (0·01 mole) in acetone (40 ml.), kept at 0°. At the end of the addition the solution was left at 0° for 3 hr. The products partly precipitated and were filtered off; the filtrate was extracted with diethyl ether. The yields were practically quantitative. *trans*-Halogenovinyl ketones (III) afforded sterically pure *trans*-sulphones (IX), and *cis*-halogenovinyl ketones (II) afforded *cis*-sulphones (VIII), with lesser amounts of *trans*-isomers (IX). The *cis*-sulphone (VIII; Ar = $C_6H_4Cl\text{-}p$) could not be isolated from the *cis–trans* mixtures obtained from *cis-p*-chlorophenyl 2-halogenovinyl ketones. Physical properties, yields, and analytical data are reported in Table 2.

(*b*) A chloroform solution of aryl 2-phenylthiovinyl ketone [*cis*-(VI) or *trans*-(VII)] was oxidised with a standard solution of perbenzoic acid (4 equiv.) in chloroform, first at −10° and then at room temperature. Completion of the reaction required 15—20 hr. Benzoic acid was removed with aqueous sodium hydrogen carbonate, and the solution was then dried and evaporated to give the sulphone. *trans*-Sulphones (IX), from *trans*-sulphides (VII), were practically pure, *cis*-sulphones (VIII), from *cis*-sulphides (VI), contained lesser amounts of *trans*-isomers (IX).

Inversion of cis-*Sulphones* (VIII) *to* trans-*Sulphones* (IX).—(*a*) A methanolic solution of *cis*-sulphone (VIII; Ar = Ph), m.p. 146—147°, was heated on a steam-bath for 20 min., in the presence of catalytic amounts of sodium methoxide. The product which separated on cooling had m.p. and mixed m.p. with the *trans*-sulphone (IX; Ar = Ph) 113° (from methanol).

(*b*) *cis*-Sulphone (VIII; Ar = Ph) was heated at 170° for 10 min. to give *trans*-sulphone (IX), m.p. 113° (from methanol).

(*c*) Under the same conditions as in (*a*) and (*b*), *trans*-sulphone (IX; Ar = Ph), m.p. 113°, remained practically unchanged. *p*-Methoxy- and *p*-chloro-derivatives (*cis* and *trans*) behaved like the non-substituted sulphones.

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