Formation and Reactivity of Thiirenium Ions [1]

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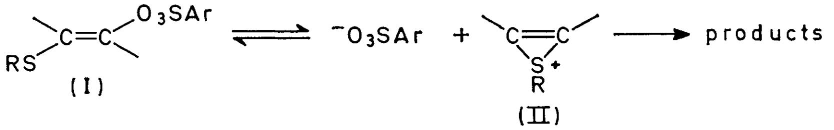
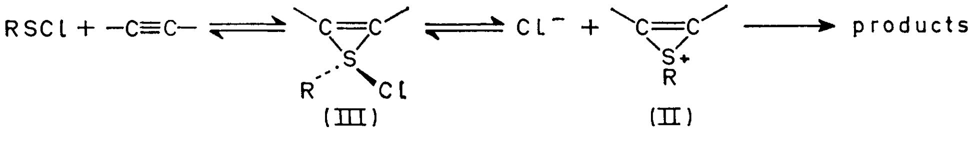
Evidence is reported that thiirenium ions are involved as intermediates in both the addition of benzenesulphenyl chloride to diarylacetylenes and in unimolecular substitution reactions of β-phenylthiovinyl sulphonates. The thiirenium ion generated from 1,2-diphenyl-2-phenylthiovinyl 2,4,6-trinitrobenzenesulphonate undergoes nucleophilic attack by chloride ion both at the carbon atoms to give 1,2-diphenyl-2-phenylthiovinyl chloride and at the sulphur atom to give diphenylacetylene and benzenesulphenyl chloride which can be trapped by added scavengers.

CHEMICAL,[2] stereochemical,[3] and kinetic data [4] indicate that the solvolysis of *trans* β-thiovinyl sulphonates (I) occurs *via* a symmetrically bridged cation, a thiirenium ion (II) [equation (1)]. Also, the addition of sulphenyl chlorides to acetylene derivatives was suggested [5] to occur *via* formation of the same cationic intermediate (II), perhaps through species (III) which has a tetra-co-ordinate sulphur atom [equation (2)]. Moreover, kinetic evidence [6] suggests that the early steps of the addition may be reversible.



(1)



(2)

Since it has been shown [2b] that esters (I; Ar = 2,4,6-trinitrophenyl) react with hydrogen chloride † in inert solvents to give β-thiovinyl chlorides, the same type of products obtained by addition of sulphenyl chlorides to

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† Chloride ions from suitable salts like tetra-alkylammonium chlorides are strong nucleophiles in inert solvents and mainly react at the aromatic nucleus of the trinitrobenzenesulphonate.

[1] (*a*) Presented in part at the IV Symposium on Organic Sulphur, Venice, June 1970; (*b*) preliminary communication, G. Scorrano and U. Tonellato, *Boll. sci. Fac. Chim. ind. Bologna*, 1969, **27**, 377.

[2] (*a*) G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2621; (*b*) p. 2625; (*c*) 1971, 3018.

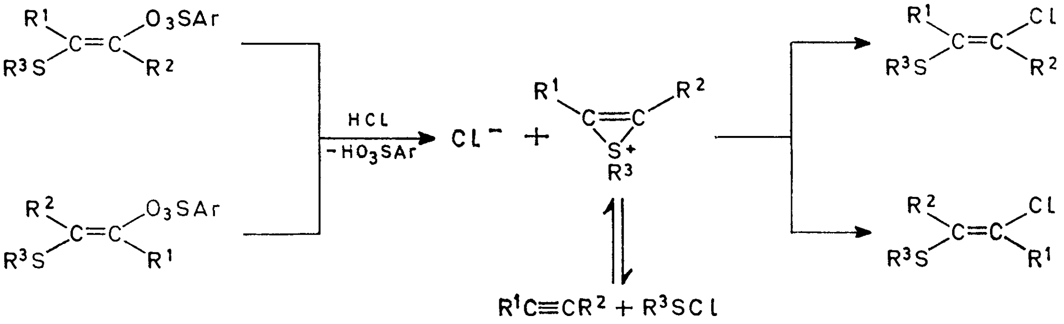
[3] G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 381.

[4] G. Modena and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 374.

[5] G. Modena and G. Scorrano in ' Mechanism of Reaction of Sulphur Compounds,' eds. N. Kharasch, B. S. Thyagarajan, and A. I. Khodair, Intra-Science Research Foundation, Santa Monica, vol. III, p. 115.

[6] A. Dondoni, G. Modena, and G. Scorrano, *Ricerca Sci.*, 1964, **34**, 665; L. Di Nunno, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Letters*, 1965, 4405.

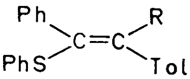
acetylene derivatives, we sought a way to confirm the hypothesis that reactions (1) and (2) occur *via* the same intermediate (II). If this is the case, the same mixture of isomeric vinyl chlorides should be obtained by reaction of unsymmetrically substituted β-thiovinyl esters with hydrogen chloride and by addition of sulphenyl chloride to the unsymmetrical cognate acetylene derivatives (Scheme). Moreover if the formation of (II) in the addition reaction is reversible, when the solvolysis of esters (I) is carried out in the presence of hydrogen chloride, some sulphenyl chloride should be freed and could be trapped by added scavengers such as reactive acetylene derivatives. The experiments would, therefore, also show that thiirenium ions, once formed, react with nucleophiles not only by attack at the ethylenic carbon atoms but also by attack at sulphur.



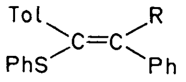
SCHEME

RESULTS

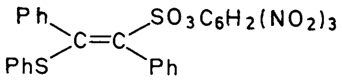
Addition of Benzenesulphenyl Chloride to Phenyl-p-*tolylacetylene* (PTA).—The addition reaction, carried out in anhydrous chloroform at 25°, affords a 3·2 (± 0·1) : 1 mixture of *trans*-2-phenyl-2-phenylthio-1-*p*-tolylvinyl chloride (IV) and *trans*-1-phenyl-2-phenylthio-2-*p*-tolylvinyl chloride (V). The ratio of the two isomers was determined by ${}^1H$ n.m.r. analysis of the crude reaction mixture and the relative abundance of the Markownikoff-type adduct is in line with the results of previous studies.[7] Vinyl chlorides (IV) and (V) easily undergo geometric isomerization in the presence of hydrogen chloride. The *trans–cis* equilibration of (IV) or (V) was not investigated in detail; however it was found that after 10 h at 25° in chloroform saturated with dry hydrogen chloride the *trans–cis* ratios were 2·1 : 1 for (IV) and 1 : 1·2 for (V).



(IV) R = Cl
(VI) R = 2,4,6-$(NO_2)_3C_6H_2SO_3$



(V) R = Cl
(VII) R = 2,4,6-$(NO_2)_3C_6H_2SO_3$



(VIII)

Reactions of 2-*Phenyl*-2-*phenylthio*-1-p-*tolylvinyl* (VI) *and* 1-*Phenyl*-2-*phenylthio*-2-p-*tolylvinyl* (VII) *Trinitrobenzenesulphonates with Hydrogen Chloride*.—The esters (VI) and (VII) were not obtained as the pure, separate isomers but as mixtures in different proportions.[3,4]

A mixture of (VI) and (VII) (3·1 : 1) reacted in chloroform saturated with hydrogen chloride at 25° for 10 h. Analysis of the products showed that the two vinyl chlorides (IV) and (V) were formed in a 3·2 (± 0·1) : 1 ratio both *trans*- and *cis*-isomers being obtained. Their ${}^1H$ n.m.r. spectra were similar to those of the mixture of (IV) and (V) obtained in the addition reaction. Experiments carried out at low conversion (after 1 h) showed that only the *trans*-isomers are initially formed; *cis*-isomerization occurs afterward. A similar reaction carried out on (VI) and (VII) (1 : 4·2) again afforded the same proportion [3·3 (± 0·1) : 1] of vinyl chlorides (IV) and (V) and the ratio of *trans* : *cis* isomers for both chlorides was virtually that observed in the previous experiment.

Reaction of 1,2-*Diphenyl*-2-*phenylthiovinyl Trinitrobenzenesulphonate* (VIII) *with Hydrogen Chloride in the Presence of Acetylene Derivatives*.—In a first set of experiments, ester (VIII) reacted with hydrogen chloride in the presence of di-*p*-tolylacetylene (DTA) used as a scavenger. The reaction was carried out in the dark at 25° until reaction was complete (10 h) (Table 1). A major feature of these experiments is the formation of 2-phenylthio-1,2-di-*p*-tolylvinyl chloride (both *trans*- and *cis*-isomers); it could not be separated from the 1,2-diphenyl-2-phenylthiovinyl chloride but was easily identified by comparison of the ${}^1H$ n.m.r. spectrum of the mixture of vinyl chlorides with those of

TABLE 1

Reactions of (VIII) with HCl in chloroform[a] containing DTA

Expt. no.[b]	Reactants (mM)	Products[c] (% yield)
1	(VIII) 1·72 DTA 1·71	Ph(PhS)C:C(Cl)Ph (58·7) Tol(PhS)C:C(Cl)Tol (7·8)
2	(VIII) 1·53 DTA 7·51	Ph(PhS)C:C(Cl)Ph (60·9) Tol(PhS)C:C(Cl)Tol (8·1)

[a] Saturated solution (150 ml). [b] Average of two runs. [c] Other products: 2,4,6-$(NO_2)_3C_6H_2{\cdot}SO_3H$ (97%), DTA, DPA (trace), Ph(PhS)CH·COPh (7%), and unidentified material.

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[7] V. Calò, G. Melloni and G. Scorrano, *Gazzetta*, 1968, **98**, 535.

authentic samples. The formation of both geometric isomers in the ratio *trans–cis* 3 : 2 is quite likely due to acid-catalysed isomerization of the *trans*-vinyl chloride (see above). The ratio of the two vinyl chlorides, the 1,2-diphenyl and the 1,2-di-*p*-tolyl is virtually the same, *ca.* 7·5 : 1, in the two experiments in spite of a five-fold increase in the molar ratio of DTA to (VIII) (see Table 1).

In a second set of experiments ester (VIII) was allowed to react with hydrogen chloride in the presence of diphenyl-[1-^{14}C]acetylene (DPA*) and *vice versa* labelled ester (VIII*) was similarly treated with unlabelled DPA. The conditions were essentially those used in the experiments of Table 1 and data are summarized in Table 2. The relative radioactivities of the 1,2-diphenyl-2-phenylthiovinyl chloride reported in Table 2 show that not all the primary product derives from ester (VIII): a fraction of it, *ca.* 10%, arises from formal transfer of the phenylthio-residue from (VIII) to the added DPA. The loss and uptake of radioactivity in the recovered DPA accord with the idea that the intermolecular transfer occurs with formation of DPA from (VIII). The agreement is more qualitative than quantitative due to the rather large errors affecting the small activity changes observed.

TABLE 2

Reactions of (VIII) with HCl in chloroform [a] containing DPA

		Products [c]	
Expt. no.[b]	Reactants (mM)	Radioactive material (% yield)	Relative molar [d] activity (%)
3	(VIII) 1·21	Ph(PhS)C:C(Cl)Ph	10·2 ± 0·3
	DPA* 4·48	DPA	97·5 ± 1
4	(VIII*) 1·02	Ph(PhS)C:C(Cl)Ph	90·2 ± 0·8
	DPA 3·72	DPA	1·40 ± 0·2

[a] Saturated solution (100 ml). [b] Average of two runs. [c] Other products: 2,4,6-$(NO_2)_3C_6H_2\cdot SO_3H$ (96%) and Ph(PhS)-CH·COPh (10—12%). [d] Relative to the specific molar radioactivity of the labelled reactant.

TABLE 3

Reactions of (VIII) with thiophenol in the presence of DPA

	Products (% yield)		
Reactants [a] (mM)	Radioactive material	Relative molar activity (%)	Other products
(VIII*) 1·72	Ph(PhS)C:C(SPh)Ph (86)	101 ± 1·5	2,4,6-$(NO_2)_3C_6H_4SO_3H$ (93)
PhSH 7·96			PhS·SPh–PhSH
DPA 3·42	DPA	0·65 ± 0·1	Ph(PhS)CH·COPh

[a] In chloroform (150 ml). [b] Relative to the specific molar activity of (VIII*).

We have also been attracted by the possibility of investigating the behaviour of (VIII) with nucleophiles other than the chloride ion. Attempts to study the reaction of (VIII) with bromide or thiocyanate ion were discouraging mainly because of the low yield of the primary substitution products. The reaction with thiophenol proved to be cleaner. Labelled ester (VIII*) was allowed to react with thiophenol in the presence of unlabelled DPA used as a carrier, in chloroform at 25° for 15 h. Table 3 shows conditions and product analysis data. Among the products, diphenyl disulphide was isolated but its yield is virtually meaningless since most of it derives from oxidation of thiophenol. The recovered DPA was slightly radioactive; the observed uptake activity would correspond to a yield in DPA from ester (VIII) of $<1·5\%$. The primary substitution product, 1,2-diphenyl-1,2-diphenylthioethylene is obtained in good yield (86%) and derives exclusively from ester (VIII).

DISCUSSION

Virtually the same proportion of β-phenylthiovinyl chlorides (IV) and (V) is obtained both in the addition of benzenesulphenyl chloride to phenyl-*p*-tolylacetylene and in the reaction of β-phenylthiovinyl esters (VI) and (VII) with hydrogen chloride. This result strongly suggests (*a*) that the addition reaction and the nucleophilic substitution involve a common intermediate in the pathway leading to products and (*b*) that such an intermediate is the bridged species (II). In fact, the α and β carbons of (VI) and (VII) lose their identity on going to products and this must occur through a geometry that symmetrizes the ethylenic structure. The present evidence, therefore, accords with the idea that a thiirenium ion is involved not only in S_N1-type reactions of β-thiovinyl derivatives (as already suggested [3,4]) but also in the electrophilic additions of sulphenyl derivatives to triple bonds (at least under the conditions used).

The reaction of the β-phenylthiovinyl ester (VIII) with hydrogen chloride in the presence of acetylenic derivatives leads to sizeable amounts of products of intermolecular transfer of the PhS residue from (VIII) to the added acetylene. Their formation is most reasonably explained by assuming nucleophilic attack of the chloride ion at the sulphur atom of the thiirenium ion. This would yield (*vide supra*) free benzenesulphenyl chloride which then adds to the acetylenic scavenger. The alternate mechanism for the formation of the products of PhS transfer involving attack of the added scavenger on the thiirenium sulphur seems highly unlikely since the amount of transfer does not change with a five-fold increase in the concentration of added scavenger (see Table 1). Therefore, the results confirm the hypothesis of the reversibility of the formation of thiirenium ions in addition of sulphenyl chlorides to triple bonds [equation (2)] and, on the whole, accord with the mechanism outlined in the Scheme.

It is interesting to compare the present results with those recently reported on the reactivity toward nucleophiles of thiiranium ions, the saturated counterparts of thiirenium ions. Helmkamp and his co-workers [8] have shown that nucleophiles such as Cl^-, Br^-, I^-, and RS^- attack exclusively the sulphonium sulphur in the case

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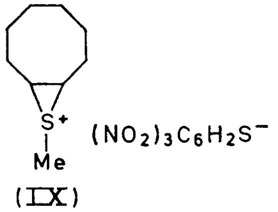
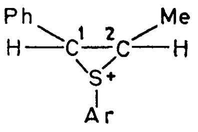
[8] D. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *J. Amer. Chem. Soc.*, 1969, **91**, 3606; D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, 1969, **91**, 5239.

of cyclo-octene *S*-methylepisulphonium ion, a stable thiiranium ion which can be isolated as a salt[9] (IX). On the other hand, Schmid and Fitzgerald,[10] evaluated the apparent relative rates of chloride ion attack at S, C-1, and C-2 of the labile thiiranium ion (X) as 1 : 120 : 2·4.



(IX)



(X)

From data of Tables 1 and 2 we can estimate that the relative rates of attack at sulphur and the carbon atoms of the thiirenium ion from ester (VIII) is *ca.* 1 : 10.

Thus the balance of sulphur *vs.* carbon attack changes greatly depending on the system investigated. Evaluation of the factors involved in the above results is a difficult task because of the different experimental conditions (solvent, sources of nucleophiles, *etc.*) used. The very large selectivity toward sulphur in Helmkamp's case is likely to be due to steric hindrance[10] to back-side attack at the carbon atoms of the eight-membered ring which is absent in acyclic compounds. However the above results indicate that the sulphur *vs.* carbon attack depends on the stability[11] of bridged ions relative to that of the corresponding open ions, in the sense that structural factors, such as the presence of *C*-aryl residues which are likely to stabilize a positive charge on a carbon atom, will favour attack at these positions. Although the exclusive *trans*-stereochemistry seemingly excludes the involvement of open ions, ring opening by nucleophilic attack in our, as well as in Schmid and Fitzgerald's, case must occur *via* a transition state in which a large fraction of the positive charge resides at the carbon atoms as indicated by the predominance in each case of Markownikoff-type products.

Finally, the results of the reaction of ester (VIII) with thiophenol indicate (see Table 3) that in this case attack on carbon is even more favoured than in that of hydrogen chloride. The result is somewhat surprising. However, examination of data on the nucleophilic reactivity in substitutions at a sulphenyl sulphur atom shows that chloride ion may be a better nucleophile than some of the so-called thiophilic ions in dipolar aprotic solvents whereas the order is dramatically inverted in protic solvents.[12] As far as the sulphur atom of the thiirenium ion resembles that of sulphenyl derivatives and the reaction medium used here is closer to a dipolar aprotic than to a protic solvent, the greater selectivity toward sulphur of hydrogen chloride than of thiophenol may be accounted for.

EXPERIMENTAL

M.p.s are uncorrected. The ^1H n.m.r. chemical shifts are given in τ values relative to tetramethylsilane. The specific activity is given in disintegrations min^{-1} mol^{-1} $\times$ 10^3. The determinations of ^{14}C content were made with a Beckman XL-100 liquid scintillation counter. The samples were dissolved in 10 ml of a toluene solution containing 0·4% of PPO and 0·01% of POPOP as scintillators. Corrections for quenching were made using a predetermined efficiency curve and the automatic external standardization mode of the counter.

Reagent grade chloroform was purified according to standard procedures shortly before use. Commercial diphenylacetylene was purified by crystallization from hexane. *trans*-1,2-Diphenyl-2-phenylthiovinyl (VIII),[13] *trans*-2-phenyl-2-phenylthio-1-*p*-tolylvinyl (VI)[4] and *trans*-1-phenyl-2-phenylthio-2-*p*-tolylvinyl (VII)[4] 2,4,6-trinitrobenzenesulphonates were prepared as described in previous papers. Di-*p*-tolylacetylene,[14] phenyl-*p*-tolylacetylene,[15] and *trans*-1,2-diphenyl-2-phenylthiovinyl chloride[2b] were prepared by literature methods. Diphenyl[1-^{14}C]acetylene was prepared from phenyl[1-^{14}C]acetic acid (Radiochemical Centre, Amersham). The labelled phenylacetic acid, diluted to the required activity, was converted to 2-phenyl-[1-^{14}C]acetophenone, as described.[2c] The latter compound (15 g) was reduced with lithium aluminium hydride (4·7 g) in dry ether (150 ml) by the usual procedure to 1,2-diphenyl-[1-^{14}C]ethanol (4·9 g, 98%), m.p. 63—65° (lit.,[16] 67°). This was dehydrated to 1,2-diphenyl[1-^{14}C]ethylene (7·2 g, 52%), m.p. 122—123° (lit.,[17] 124·5—124·8°), by vacuum distillation in the presence of a few drops of conc. sulphuric acid. Bromination of the labelled stilbene (6·1 g) in dry ether afforded 1,2-dibromo-1,2-diphenyl[1-^{14}C]ethane (7·8 g, 68%), m.p. 238—241° (lit.,[18] 243—244°). The dibromide (6·8 g) was treated with potassium hydroxide (7·5 g) in absolute ethanol (30 ml) at reflux for 24 h, the mixture was then poured into water, and the solid diphenyl[1-^{14}C]acetylene was filtered and purified by column chromatography on silica gel with light petroleum–ether eluant (2·9 g, 82%), m.p. 57—58° (lit.,[19] 56—57°).

1,2-Diphenyl-2-phenylthio[^{14}C]vinyl 2,4,6-trinitrobenzenesulphonate, m.p. 109° (lit.,[13] m.p. 109—110°), was obtained from the labelled diphenylacetylene and benzenesulphenyl trinitrobenzenesulphonate as described.[13]

Addition of Benzenesulphenyl Chloride to Phenyl-p-*tolylacetylene* (PTA).—The sulphenyl chloride (5·0 g) in chloroform (50 ml), was added dropwise to a solution of PTA (7·3 g) in chloroform (100 ml). The resulting solution, after standing overnight at 25°, was washed (water, dilute $NaHCO_3$ solution, water) and dried (Na_2SO_4). Evaporation left a solid residue which was chromatographed on silica gel with light petroleum–ether as eluant. The excess of PTA

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[9] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, 1963, **28**, 2932; 1964, **29**, 2702.

[10] G. H. Schmid and P. H. Fitzgerald, *J. Amer. Chem. Soc.*, 1971, **93**, 2547.

[11] G. Capozzi, G. Modena, and U. Tonellato, *J. Chem. Soc.* (*B*), 1971, 1700; A. Burighel, G. Modena, and U. Tonellato, *Chem. Comm.*, 1971, 1325; *J.C.S. Perkin II*, 1972, 2026.

[12] J. L. Kice and G. B. Large, *J. Amer. Chem. Soc.*, 1968, **90**, 4069, and references therein.

[13] G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc.* (*C*), 1970, 2617.

[14] T. Curtius and R. Kastner, *J. prakt. Chem.*, 1911, **83**, 215.

[15] G. Drefahl and G. Plotner, *Chem. Ber.*, 1958, **91**, 1274.

[16] W. Gerrard and J. Kenyon, *J. Chem. Soc.*, 1928, 2564.

[17] R. H. Smith and D. H. Andrews, *J. Amer. Chem. Soc.*, 1931, **53**, 3644.

[18] L. I. Smith and H. H. Hoehn, *J. Amer. Chem. Soc.*, 1941, **63**, 1180.

[19] J. G. Burr, jun., *J. Amer. Chem. Soc.*, 1953, **75**, 1990.

was separated from a mixture of the two isomers 2-phenyl-2-phenylthio-1-*p*-tolylvinyl (IV) and 1-phenyl-2-phenylthio-2-*p*-tolylvinyl chlorides (V) (10·6 g, 90%) (Found: C, 74·6; H, 5·1; Cl, 10·7. Calc. for $C_{21}H_{17}ClS$: C, 74·85; H, 5·1; Cl, 10·5%), τ (CS_2) 2·5—3·1 (14H, m) and 7·65 and 7·75 (total 3H, relative ratio 1 : 0·31). The major *component* (IV) was isolated by means of fractional crystallization from methanol, m.p. 91—92° (Found: C, 74·6; H, 5·0; Cl, 10·55%).

A portion of the original mixture of (IV) and (V) was dissolved in chloroform saturated with hydrogen chloride and the solution was kept at 25° for 10 h. The mixture of vinyl chlorides recovered as described below had τ (CS_2) 2·5—3·2 (14H, m) and 7·65, 7·75, 7·82, and 7·92 (total 3H, s, relative ratios, 1 : 0·2 : 0·45 : 0·25). The new signals at τ 7·82 and 7·92 are consistent with the formation of the *cis*-isomers of (IV) and (V) respectively.

Reaction of Esters (VI) *and* (VII) *with Hydrogen Chloride.*—(*a*) A mixture of (VI) and (VII) (3·1 : 1; 0·419 g) was dissolved in chloroform (50 ml). The solution was saturated with hydrogen chloride and kept in the dark for 10 h at 25°. The excess of hydrogen chloride was then pumped off and the precipitated solid was filtered. It was identified as 2,4,6-trinitrobenzenesulphonic acid (0·203 g, 96%). The filtered solution was evaporated to dryness under reduced pressure and the residue chromatographed on silica gel using n-hexane–benzene (19 : 1) as eluant. Besides minor amounts of unidentified material, a mixture of vinyl chlorides was isolated, τ (CS_2) 2·5—3·2 (14H, m) and 7·66, 7·75, 7·81, and 7·92 (total 3H, s, relative ratios 1 : 0·21 : 0·47 : 0·25) corresponding (see above) to a 3·2 : 1 mixture of (IV) and (V) both in the *cis*- and *trans*-forms (0·171 g, 72%) (Found: C, 75·1; H, 5·3; Cl, 10·8%). When a mixture of (VI) and (VII) of the same ratio was treated as above and the products analysed after only 1 h, the product, isolated as above, had a ^1H n.m.r. spectrum corresponding to the *trans*-forms of the two structural isomers. Only when the mixture was analysed after 4 h were signals at τ 7·81 and 7·92 observed.

(*b*) From a mixture of (VI) and (VII) (1 : 4·2; 0·392 g) in chloroform (50 ml), by procedure (*a*), the mixture of vinyl chlorides isolated had τ 2·5—3·1 (14H), 7·66, 7·75, 7·81, and 7·92 (total 3H, relative ratios 1 : 0·19 : 0·42 : 0·24) corresponding to a 3·3 : 1 mixture of (IV) and (V) (0·151 g, 68%).

Reactions of Ester (VIII) *with Hydrogen Chloride.*—*Experiment* 1 (*Table* 1). Ester (VIII) (1·00 g) and DTA (0·353 g) were dissolved in chloroform (150 ml) and the solution was saturated with dry hydrogen chloride. The flask was stoppered and left in the dark at 25° for 10 h. By the same procedure described above, besides the sulphonic acid (0·507 g, 99%), the following fractions were isolated and identified: (*a*) a mixture of diphenylacetylene and diphenyl disulphide (0·02 g, *ca.* 1 : 1; i.r.), (*b*) DTA (0·319 g, 91% recovered; n.m.r.), (*c*) a mixture of vinyl chlorides, τ (CS_2) 2·5—3·1 (20·9H, m) and 7·65, 7·76, 7·79, and 7·91 (1H, methyl region, ratios 1·5 : 1·5 : 1 : 1) corresponding to a 7·5 : 1 mixture of 1,2-diphenyl-2-phenylthiovinyl chloride (59%) and 2-phenylthio-1,2-di-*p*-tolylvinyl chloride (8%). A 7·5 : 1 mixture of authentic *trans*-chlorides was left in chloroform saturated with hydrogen chloride at 25° for 10 h and gave a ^1H n.m.r. spectrum virtually superimposable on that of the mixture (*c*). Attempts to separate the two chlorides by crystallization from ethanol led only to the isolation of 1,2-diphenyl-2-phenylthiovinyl chloride, m.p. 92·5—93° (lit.,[2b] 93—94°), and (*d*) 2-phenyl-2-(phenylthio)acetophenone (0·040 g, 7·5%; i.r.).

Experiment 2 (*Table* 1). Ester (VIII) (0·887 g) and DTA (1·55 g) were dissolved in chloroform (150 ml) and treated as above. The following products were isolated and identified: trinitrobenzenesulphonic acid (0·435 g, 95%); DTA (1·42 g, 91·5% recovered), a mixture of vinyl chlorides (0·344 g), τ (CS_2) 2·5—3·1 (21·2H, m) and 7·66, 7·77, 7·80, and 7·91 (1H, methyl region), comprising 1,2-diphenyl- and 1,2-di-*p*-tolyl-2-phenylthiovinyl chlorides (7·6 : 1), and 2-phenyl-2-(phenylthio)acetophenone (0·03 g, 6·6%).

Experiment 3 (*Table* 2). Ester (VIII) (0·700 g) and labelled DPA (0·801 g) with an activity of 582·4 were dissolved in chloroform (100 ml) and treated as above. The following products were isolated: trinitrobenzenesulphonic acid (0·348 g, 96%), DPA (activity 567·8), 1,2-diphenyl-2-phenylthiovinyl chloride (0·251 g, 63·3%; m.p. 87—89°); on recrystallization from ethanol it had an activity of 59·4, 2-phenyl-2-(phenylthio)acetophenone (0·045 g, 12·2%), and a viscous yellow material (0·03 g) which was not identified.

Experiment 4 (*Table* 2). Labelled ester (VIII) (0·591 g) with an activity of 580·5 and DPA (0·663 g) were dissolved in chloroform (100 ml) and treated as above. The products isolated and identified were trinitrobenzenesulphonic acid (0·291 g, 95%), DPA (0·610 g, 92% recovered; activity 8·13), 1,2-diphenyl-2-phenylthiovinyl chloride (0·201 g, 61%; activity 523·0), and 2-phenyl-2-(phenylthio)acetophenone (0·032 g, 10·3%).

Reaction of Ester (VIII) *with Thiophenol.*—Labelled ester (VIII) (1·00 g) with an activity of 580·5, thiophenol (0·97 g), and DPA (0·609 g) were dissolved in chloroform (150 ml). After 15 h the mixture was analysed as described above. Besides the sulphonic acid (0·48 g, 93%), the following fractions were isolated by column chromatography: (*a*) a mixture of diphenyl disulphide, thiophenol, and DPA (0·80 g; i.r.). Attempts to separate DPA from the disulphide by chromatography or fractional crystallization were unsuccessful. The mixture was therefore heated at reflux for 3 h in 5% sodium hydroxide in ethanol–water (7 : 3) and then extracted with ether. The organic layer was dried (Na_2SO_4) and the solvent was evaporated. From the residue, DPA was obtained, by repeated elution through silica gel using hexane as eluant, with activity 5·77 and (*b*) 1,2-diphenyl-1,2-diphenylthioethylene (0·590 g, 86·4%), m.p. 160—161° (from ethanol) (lit.,[20] 160—162°), activity 586·3.

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[20] T. Posner, *Chem. Ber.*, 1902, **35**, 506.