

Reactivity of Vinyl Sulphonic Esters. Part XIV.¹ Addition of Trinitrobenzenesulphonyl Hypohalites to Acetylene Derivatives to give β -Halogenovinyl Sulphonates

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The synthesis of several β -halogenovinyl 2,4,6-trinitrobenzenesulphonates. $R^2(\text{Hal})\text{C}:\text{C}(\text{O}_3\text{STnp})\text{R}^1$ (Hal = Cl, Br, or I) by addition of trinitrobenzenesulphonyl hypohalites to substituted diphenylacetylenes or alkynes is reported. The stereochemistry and orientation of the addition are discussed in terms of the structure of the vinyl cation intermediate, which may be either bridged or open depending on the nature of the halogens and of the residues R^2 and R^1 linked to the unsaturated system.

VINYL cations are generally represented ² as open digonal structures (I). However, extensive studies on

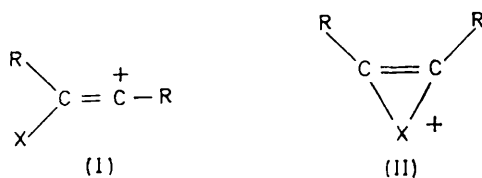
¹ Part XIII, A. Burighel, G. Modena, and U. Tonellato, *J.C.S. Perkin II*, 1972, 2026.

² R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1969, **91**, 5350; A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, 1971, **55**, 3835.

electrophilic additions of sulphenyl derivatives to acetylenes ³ and on S_N1 reactions of *trans*- β -thiovinyl

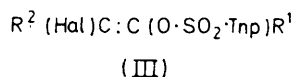
³ G. Modena and G. Scorrano in ' Mechanism of Reactions of Sulfur Compounds,' ed. N. Kharash, B. S. Thyagarajan, and A. I. Khodair, Intra Science Foundation, Santa Monica, 1969, vol. III, p. 115; G. Scorrano and U. Tonellato, *Bull. sci. Fac. Chim. ind. Bologna*, 1969, **27**, 377.

sulphonates^{1,4} clearly indicate that a bridged structure (II; X = SR or ArS) rather than an open one (I) is

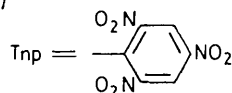


a better representation of the cationic intermediate involved in such processes. Moreover, recent reports on the electrophilic addition of bromine⁵ or pseudo-halogens⁶ such as iodine azide to acetylene derivatives suggest that the vinyl cations thus generated may have a bridged geometry (II) alternative to the open one (I).

Further information on the nature of the unsaturated cation formed by addition of positive halogen to a triple bond is presented here. The reaction actually investigated was the addition of 2,4,6-trinitrobenzenesulphonyl hypohalites to acetylene derivatives to give



Hal = a: I b: Br c: Cl

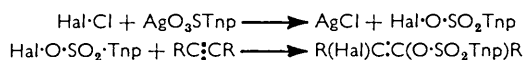


β -halogenovinyl trinitrobenzenesulphonates (III). The esters (III) have been designed primarily for the study⁷ of the effect of β -halogens in S_N1 -type vinylic reactions.

RESULTS AND DISCUSSION

Synthesis.—The esters (IIIa–c) were synthesised by reactions of chlorine, bromine chloride, and iodine chloride, respectively, with silver trinitrobenzenesulphonate and the appropriate acetylene derivative in anhydrous dichloromethane. The reactions were carried out in the dark under nitrogen at *ca.* 0°, and usually required 30 min to 4 h.

The halogens and interhalogen compounds probably react with the silver sulphonate to give sulphonyl hypohalite, which then by electrophilic addition to the triple bond gives a 1:1 adduct. Attempts to isolate



or identify the sulphonyl hypohalites were unsuccessful since they readily decompose. Their formation is suggested by analogy with the sequence proposed⁸ for the addition of sulphenyl sulphonates to acetylenes to give β -thiovinyl sulphonates, and is consistent with the structure of the products isolated (see later).

The yields of crude products (IIIa and b) were 75–80% or higher; the remainder was mostly tarry ma-

terial and, in some cases, unchanged acetylene derivative. In the addition of sulphonyl hypochlorite, the yields of products (IIIc) were considerably lower (40–60%) because of side reactions. These were not investigated in detail; however products of addition of chlorine to the triple bond were obtained in some cases. The low yields of (IIIc) may be due to the fact that the reactions of chlorine with the acetylene derivatives and with the silver sulphonate are concurrent processes or that the sulphonyl hypochlorite is particularly unstable. The purified esters (III) showed spectral and other physical properties characteristic⁸ of covalent vinyl sulphonates and were obtained in reasonable overall yields (see Experimental section). Control experiments showed that, with the exception of the most reactive⁷ esters (IIIa; R¹ = R² = *p*-tolyl; R¹ = *p*-tolyl, R² = Ph) which partly decompose with formation of free iodine, all compounds (III) synthesised are stable and, in particular, do not isomerize (as revealed by ¹H n.m.r. analysis) under the reaction conditions.

An alternative procedure for the synthesis of esters (IIIb and c) was explored but the results were not encouraging. *N*-Bromosuccinimide was found to react in the presence of trinitrobenzenesulphonic acid with diarylacetylenes in dichloromethane at 0° to give esters (IIIb; R¹ and R² = Ar) in modest yield. On the other hand, under the same conditions, *N*-chlorosuccinimide does not give appreciable amounts of esters (IIIc).

Stereoselectivity and Regioselectivity.⁹—(a) *Addition to diarylacetylenes.* In the simple case of addition of sulphonyl hypohalites to symmetrically substituted acetylenes only geometric isomers can be formed. ¹H N.m.r. analysis of the crude reaction mixtures (see Experimental section) obtained from symmetrical diarylacetylenes showed that in the case of β -iodo-derivatives (IIIa) only one isomer is formed, whereas in the case of β -bromo- (IIIb) and β -chloro-vinyl esters (IIIc) both *trans*- and *cis*-isomers are obtained although in different proportions.

To the one geometric isomer obtained in the case of β -iodovinyl esters, the *trans*-geometry can be reasonably assigned on the following grounds. (i) The additions of alkane- or arene-sulphenyl sulphonates to acetylene derivatives^{8,10} and of acetyl hypoiodite to diphenylacetylene¹¹ are also highly stereoselective and afford *trans*-1,2-adducts. (ii) 2-Iodo-1,2-diphenylvinyl trinitrobenzenesulphonate reacts in acetic acid at 25° to give 2-iodo-1,2-diphenylvinyl acetate (83%) exclusively (>97% by ¹H n.m.r.) in the *trans* form¹⁰ under kinetic control. Since available kinetic evidence indicates a unimolecular mechanism for the acetolysis,⁷

⁷ Preliminary report, P. Bassi and U. Tonellato, *Gazzetta*, 1972, **102**, 387.

⁸ G. Capozzi, G. Melloni, and G. Modena, *J. Chem. Soc. (C)*, 1970, 2617.

⁹ A. Hassner, *J. Org. Chem.*, 1968, **33**, 2684.

¹⁰ M. Meyers and K. N. Trueblood, *Acta Cryst.*, 1969, *B*, **25**, 2588.

¹¹ Y. Ogata and I. Urasaki, *J. Org. Chem.*, 1971, **36**, 2164.

⁴ G. Capozzi, G. Modena, G. Melloni, and U. Tonellato, *Chem. Comm.*, 1969, 1520; G. Modena and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 374, 1569.

⁵ J. A. Pincock and K. Yates, *Canad. J. Chem.*, 1970, **48**, 3332.

⁶ A. Hassner, R. J. Ibister, and A. Friederang, *Tetrahedron Letters*, 1969, 2939.

the complete stereospecificity can only be explained¹² in terms of retention of the *trans*-configuration by assuming a bridged geometry (II; X = I) for the intermediate cation. (iii) Esters (IIIa) react under solvolytic conditions⁷ much faster than the analogous β -bromo- and γ -chloro-vinyl esters, a fact which suggests effective anchimeric assistance due to the β -iodine atom. Such effects require that the iodine be *trans* to the leaving group.

On the other hand, consistent with this reasoning, the high degree of stereoselectivity may be taken as evidence of the intermediacy of bridged cations (II) in the formation of β -iodovinyl esters (IIIa).

On this basis and on the assumption that the effect of changing the β -halogen in otherwise structurally similar esters (IIIa), (IIIb), and (IIIc) does not appreciably effect the chemical shifts of the *meta*-protons of the trinitrobenzenesulphonate group and those of the

(b) *Addition to dialkylacetylenes.* Addition to but-2-yne or oct-4-yne apparently affords one isomer only, since only one signal, τ 1.30 \pm 0.03 (in the region of the *meta*-protons of the trinitrobenzenesulphonate group) is observed in each case in the ¹H n.m.r. spectra of the crude products.

In the synthesis of β -chlorovinyl esters (see before) the formation of a complex mixture of variable composition which accompanies the vinyl ester does not allow evaluation by ¹H n.m.r. analysis of whether minor amounts of the other isomer are also formed but, in each run, only one isomer was isolated by normal work-up.

On the basis of the foregoing arguments, the *trans*-structure can be reasonably assigned to the isomer formed; the addition to dialkylacetylenes thus appears to be in each case highly *trans* stereoselective.

(c) *Addition to unsymmetrical diarylacetylenes.* The

TABLE I
Significant chemical shifts of *trans*- and *cis*-isomers of esters (III) in CDCl₃

Ester	R ¹	R ²	τ_{m-H} ^a		τ_{p-CH_3} ^b		Ratio ^c <i>trans</i> : <i>cis</i>
			<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	
(IIIa)	Ph	Ph	1.66				> 20 †
(IIIa)	<i>p</i> -tolyl	Ph	1.68		7.64		> 20 †
(IIIa)	<i>p</i> -tolyl	<i>p</i> -tolyl	1.66		7.62—7.82		> 20 †
(IIIb)	Ph	Ph	1.67	1.40			8
(IIIb)	<i>p</i> -tolyl	Ph	1.67	1.39	7.63	7.75	8
(IIIb)	<i>p</i> -tolyl	<i>p</i> -tolyl	1.66	1.39	7.62—7.81	7.76—7.69	7.5
(IIIc)	Ph	Ph	1.64	1.40			0.7
(IIIc)	<i>p</i> -tolyl	Ph	1.65	1.39	7.63	7.77	0.65
(IIIc)	<i>p</i> -tolyl	<i>p</i> -tolyl	1.67	1.39	7.62—7.81	7.76—7.69	0.65
(IIIc)	<i>p</i> -MeO·C ₆ H ₄	<i>p</i> -MeO·C ₆ H ₄	1.67	1.38			0.6

^a Chemical shifts (\pm 0.02 p.p.m.) of the *meta*-protons of the 2,4,6-trinitrobenzenesulphonate group. ^b Chemical shifts (\pm 0.02 p.p.m.) of the *para*-methyl protons of the tolyl residues when present. ^c From the integral ratios of the signals at τ_{m-H} (and τ_{p-CH_3}) assigned to the two isomers.

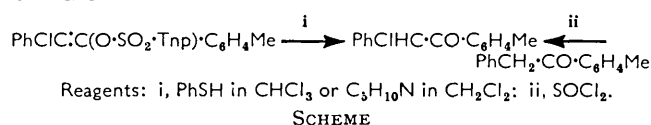
† Within the detectability limits of the ¹H n.m.r. analysis.

para-methyl protons in di-*p*-tolyl or phenyl-*p*-tolyl derivatives, the ¹H n.m.r. data reported in Table I allow an evaluation of the relative yields of *trans*- and *cis*-isomers in some typical cases.

The case of di-*p*-tolylacetylene illustrates the stereochemistry of the addition of sulphonyl hypobromite and hypochlorite (see Table I). The *trans*- β -bromovinyl ester is obtained in much greater yield than the *cis*-isomer. The *trans*-form can be easily separated by crystallization from dichloromethane-pentane whereas a 1:1 mixture of the two isomers is obtained from the mother liquors of repeated crystallizations from the above solvent mixture. The *trans*-isomer reacts in acetic acid faster than the *cis*: by controlled destruction of the former in a 1:1 mixture, virtually pure *cis*-ester was isolated and characterized. On the other hand, the β -chlorovinyl ester is obtained mainly in the *cis*-form. This isomer can be separated by crystallization of the crude material and a 1:1 mixture of the two isomers is recovered from the mother liquors of repeated crystallizations. Attempts to separate the *trans*-ester have not yet succeeded because the two geometric isomers react at virtually the same rate under solvolytic conditions.

addition of trinitrobenzenesulphonyl hypiodite to phenyl-*p*-tolylacetylene, which is expected to be highly *trans* stereoselective, affords one structural isomer in much greater yield (at least 10:1) than the other possible isomer. In the case of additions of hypobromite or hypochlorite to phenyl-*p*-tolylacetylene the reaction is apparently even more regioselective.

The major structural isomer is the Markownikoff adduct, *i.e.* the 2-halogeno-2-phenyl-1-*p*-tolylvinyl sulphonate. The β -chlorovinyl ester reacts with benzenethiol or piperidine *via* nucleophilic aromatic substitution at the trinitrobenzene ring⁸ to give 2-chloro-2-phenyl-*p*-methylacetophenone, identified as indicated in the Scheme.

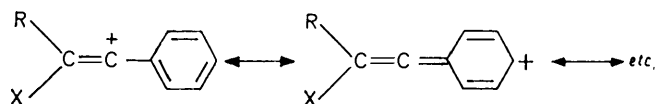


General.—The results agree with the idea that the key step of the reaction is the electrophilic addition of positive halogen to the triple bond. This is indicated

¹² Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1969, **91**, 6734.

by the high degree of regioselectivity, which demands that the product-determining step is a nucleophilic attack of sulphonate anion on a vinyl cation intermediate.

On the other hand, the remarkable differences in the stereochemical outcome of the reaction suggest that the geometry of the vinyl cation may change depending on both the nature of the halogen and that of the acetylene derivative. In the addition to diarylacetylenes, a gradual shift from a bridged (II) to an open (I) species on going from iodine to bromine and chlorine is apparent. In the addition to dialkylacetylenes the bridged geometry is, in the light of all the evidence, more favoured than the open one, irrespective of the nature of the halogen. A similar trend was observed by Pincock and Yates:⁵ whereas the addition of bromine to arylacetylenes in acetic acid is not stereoselective, the corresponding addition to dialkylacetylenes is entirely *trans* stereoselective. This is not surprising in view also of the evidence obtained in the case of thiovinyl cations. An open cation (I; X = SR or SAr) bearing an α -aryl residue is much more effectively stabilized by resonance than an α -alkyl cation of the same geometry,⁴ whereas the same change is not expected sensibly to affect the stability of bridged ions.¹³ Thus apparently, open cations (I; X = Hal) will be more



stable than the bridged forms if both the following conditions are met: (i) the presence of aryl residues linked to an unsaturated carbon atom, and (ii) a poorly effective bridging halogen.

The high degree of regioselectivity resulting in the additions to acetylenes of type $\text{Ar}^1\text{C}\equiv\text{CAr}^2$ is similar to that previously observed when benzenesulphenyl trinitrobenzenesulphonate was used;¹⁴ it was suggested that in such cases $\text{S}_{\text{N}}1$ -type ring opening of a bridged cation (II) may precede reaction with the nucleophile.

EXPERIMENTAL

Chemical shifts are relative to tetramethylsilane for solutions in deuteriochloroform. But-2-yne, oct-4-yne and diphenylacetylene were commercial products. Di-*p*-tolylacetylene,¹⁵ di-*m*-tolylacetylene,¹⁶ phenyl-*p*-tolylacetylene,¹⁷ *p*-chlorophenyl(phenyl)acetylene,¹⁸ and 2,4,6-trinitrobenzenesulphonic acid and its silver salt¹⁹ were prepared by literature methods. Bromine chloride and iodine chloride solutions in dichloromethane were prepared by mixing equimolar amounts of the appropriate halogens shortly before use.

Synthesis of the Esters (III).—The appropriate acetylene derivative (5 mmol) and silver trinitrobenzenesulphonate (6 mmol) were added to anhydrous dichloromethane (120

ml). To the resulting suspension cooled at -5° , kept under nitrogen and protected from light, the halogen or interhalogen compound (5 mmol) solution in dichloromethane (20–30 ml) was added dropwise. The mixture was stirred for 2–4 h and then warmed to room temperature. Shorter reaction times (30 min to 1 h) were required for the addition of sulphonyl hypochlorite to diarylacetylenes: in the particular case of addition to di-*p*-methoxyphenylacetylene the reaction is conveniently stopped just after mixing of the reagents. The solution was filtered, the solvent removed under reduced pressure, and the crude residue, dissolved in deuteriochloroform, was analysed for isomeric composition of the resulting ester (III) by ^1H n.m.r. spectroscopy (signals, τ 1.2–1.8, due to the *meta* protons of the trinitrophenyl group). The crude mixture was then either repeatedly crystallised from dichloromethane–pentane or, dissolved in dichloromethane, percolated through a short silica gel column and recrystallised until satisfactory elemental analyses were obtained. The overall yields after purification were 55–63% for esters (IIIa) and (IIIb) and 30–50% for esters (IIIc). Physical and analytical data are reported in Table 2. Most esters melted with darkening and decomposition. 1,2-Diaryl derivatives are orange-yellow and 1,2-dialkyl derivatives pale yellow; with the exception of some of the β -iodovinyl esters, all the compounds listed in Table 2 are stable at room temperature if protected from light. The specific conductance of all esters (III), as measured in nitromethane at 25° , is $1\text{--}5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. In the case of esters (IIIa; $\text{R}^1 = \text{R}^2 = \text{Ar}$) the specific conductance increases with time since they decompose to give trinitrobenzenesulphonic acid.^{7,8} Common characteristic i.r. absorption bands⁸ (solid, KBr) are observed at 3100–3085, 1560–1550, 1360–1340, 1200–1190, and 760–750 cm^{-1} .

Synthesis of the Esters (IIIb; $\text{R}^1 = \text{R}^2 = \text{Ar}$) with *N*-Bromosuccinimide (NBS).—A mixture of diarylacetylene (5 mmol), trinitrobenzenesulphonic acid (8 mmol), and NBS (5 mmol) in anhydrous dichloromethane (200 ml), kept at 0° under nitrogen, was stirred for 2 h, then warmed to room temperature, percolated through a short silica gel column, and evaporated under reduced pressure. Crystallization of the residue from dichloromethane afforded *trans*-1,2-diaryl-2-bromovinyl esters (10–15%) identical with those obtained by the method previously described.

Separation of *trans*- and *cis*-2-Bromo-1,2-di-*p*-tolylvinyl 2,4,6-Trinitrobenzenesulphonates.—The crude product obtained by addition of sulphonyl hypobromite to di-*p*-tolylacetylene, identified as a 7 : 1 mixture of *trans*- and *cis*-isomers, was twice recrystallised from dichloromethane–pentane to give the *trans*-isomer in pure form (at least 93% by ^1H n.m.r. and at least 97% by kinetic analysis). Fractional crystallisations of the mother liquor content led to a 1 : 1 mixture of the two isomers, the composition of which did not appreciably change on further recrystallisations. Such a mixture was heated at 80° in acetic acid for the time evaluated for complete solvolysis (*ca.* 6 half-lives) of the *trans*-ester. The solution was then poured into dichloromethane–water and exhaustively washed with sodium carbonate solution and water; the organic layer was dried (Na_2SO_4), evaporated to a small

¹³ G. Capozzi, G. Modena, and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 1700.

¹⁴ G. Modena and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 381.

¹⁵ T. Curtius and R. Kastner, *J. prakt. Chem.*, 1911, **83**, 215.

¹⁶ G. H. Coleman, W. H. Holst, and R. D. Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 2310.

¹⁷ G. Drefahl and G. Plotner, *Chem. Ber.*, 1958, **91**, 1274.

¹⁸ M. S. Newman and D. S. Reid, *J. Org. Chem.*, 1958, **23**, 665.

¹⁹ D. J. Pettit and G. K. Helmkamp, *J. Org. Chem.*, 1969, **29**, 2702.

volume, and treated with pentane. The yellow precipitate appeared to be a pure isomer (at least 93% by ^1H n.m.r. analysis). Its i.r. spectrum resembled that of the *trans*-isomer except for alterations in the intensity and shape of bands around 1400, 1200, and 840—700 cm^{-1} .

[9:1 hexane-benzene as eluant] gave the title ketone (0.21 g, 76%) whose ^1H n.m.r. [τ 2.0—2.2 (2H, d), 2.3—3.0 (7H, m), 3.56 (1H, s), and 7.77 (3H, s)], i.r., and u.v. spectra were identical with those of an authentic sample prepared²⁰ from benzyl tolyl ketone and sulphuryl chloride.

TABLE 2
Physical and analytical data for β -halogenovinyl esters (III)

Ester	R ¹	R ²	Geo- metry ^a	M.p. (°C)	Found (%)						Calc. (%)					
					C	H	N	S	I	Cl	C	H	N	S	I	Cl
(IIIa)	Me	Me ^b	T	139—140	25.15	1.65	9.0	6.7	26.6		25.4	1.7	8.85	6.75	26.8	
(IIIa)	Pr ⁿ	Pr ⁿ ^c	T	92—94	31.65	3.0	7.85	6.2	23.75		31.75	3.05	7.95	6.15	24.0	
(IIIa)	Ph	Ph	T	142—143	40.45	1.95	6.95	5.35	21.35		40.2	2.0	7.05	5.35	21.25	
(IIIa)	<i>p</i> -Tolyl	<i>p</i> -Tolyl	T	108—110	41.0	2.35	6.5	5.35	20.5		42.65	2.6	6.7	5.15	20.3	
(IIIa)	<i>p</i> -Tolyl	Ph	T	112	41.05	2.55	7.0	5.25	20.5		41.25	2.3	6.85	5.25	20.75	
(IIIa)	<i>m</i> -Tolyl	<i>m</i> -Tolyl	T	127	41.95	2.65	6.7	5.3	20.5		42.25	2.6	6.7	5.15	20.3	
(IIIa)	Ph	<i>p</i> -ClC ₆ H ₄	T	127—129	37.75	1.6	6.70	5.1	19.9	5.55	38.0	1.75	6.65	5.05	20.1	5.6
					C	H	N	S	Br	Cl	C	H	N	S	Br	Cl
(IIIb)	Me	Me ^d	T	140.5—141	28.2	2.05	9.75	7.6	18.75		28.2	1.9	9.85	7.5	18.75	
(IIIb)	Pr ⁿ	Pr ⁿ ^e	T	67—68	34.65	3.45	8.7	6.7	16.6		34.8	3.3	8.7	6.65	16.6	
(IIIb)	Ph	Ph	T	138—139	43.85	2.25	7.7	5.9	14.6		43.6	2.2	7.6	5.8	14.5	
(IIIb)	<i>p</i> -Tolyl	<i>p</i> -Tolyl	T	144	45.9	2.8	7.2	5.45	14.05		45.7	2.8	7.25	5.55	13.8	
(IIIb)	<i>p</i> -Tolyl	<i>p</i> -Tolyl	C	152—153	45.95	2.8	7.05	5.75	14.0		45.7	2.8	7.25	5.55	13.8	
(IIIb)	<i>p</i> -Tolyl	Ph	T	134—136	44.9	2.35	7.35	5.7	14.35		44.7	2.5	7.45	5.7	14.2	
(IIIb)	<i>m</i> -Tolyl	<i>m</i> -Tolyl	T	144—145	45.35	2.7	7.0	5.55	14.0		45.7	2.8	7.25	5.55	13.8	
(IIIc)	Me	Me ^f	T	118—120	31.25	2.0	10.75	8.2		9.05	31.45	2.1	11.0	8.4		9.3
(IIIc)	Ph	Ph	C	148	47.3	2.2	8.15	6.05		7.2	47.5	2.4	8.3	6.3		7.0
(IIIc)	Ph	Ph	C + T		47.2	2.35	8.2	6.15		7.1	47.5	2.4	8.3	6.3		7.0
(IIIc)	<i>p</i> -Tolyl	<i>p</i> -Tolyl	C	158—160	49.75	3.1	7.85	6.05		6.75	49.5	3.0	7.85	6.0		6.65
(IIIc)	<i>p</i> -Tolyl	<i>p</i> -Tolyl	C + T		49.7	2.8	7.8	6.1		6.85	49.5	3.0	7.85	6.0		6.65
(IIIc)	<i>p</i> -Tolyl	Ph	C	147—148	48.35	2.8	8.05	6.25		7.0	48.5	2.7	8.1	6.15		6.8
(IIIc)	<i>p</i> -MeO-C ₆ H ₄	<i>p</i> -MeO-C ₆ H ₄	C	129—130	46.5	2.65	8.15	5.75		6.5	46.7	2.85	7.4	6.65		6.25

^a C = *cis*; T = *trans*. C + T refers to a ca. 1:1 mixture of *cis*- and *trans*-isomers. ^b τ 1.31 (2H, s) 7.56br (3H, s), and 7.65br (3H, s). ^c τ 1.30 (2H, s) 7.35 (2H, t), 7.41 (2H, t), ca. 8.4 (4H, m), and 9.0 (6H, double t). ^d τ 1.31 (2H, s) and 7.71br (6H, s). ^e τ 1.31 (2H, s), 7.25 (2H, t), 7.50 (2H, t), ca. 8.5 (4H, m), and 9.0 (6H, double t). ^f τ 1.30 (2H, s) and 7.85 (6H, two unresolved broad s).

Conversion of 2-Chloro-2-phenyl-1-*p*-tolylvinyl Trinitrobenzenesulphonate into 2-Chloro-2-phenyl-*p*-methylacetophenone.—Benzenthionol (0.40 g) and the title ester (0.59 g) dissolved in chloroform (100 ml) were heated at 80° for 2 h in a sealed vial. The solution was then poured into water and the organic layer washed with water and dried (Na₂SO₄). Chromatography of the residue on a silica gel column

The conversion (75%) was also achieved by treating the vinyl ester with piperidine in dichloromethane at reflux for 1 h.⁸

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²⁰ R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, 1963, **85**, 820.