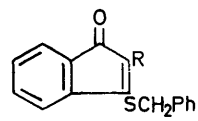
Reactions of β-Benzylthio- and β-Benzylsulphonyl-cinnamic Acids and Esters

By **K. Buggle, E. M. Philbin, and N. D. Ryan,** Department of Chemistry, University College, Belfield, Dublin 4, Ireland

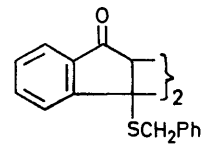
Configurations have been assigned to the title compounds from their n.m.r. spectra. Cyclisation of *cis*- and *trans*-β-(benzylthio)cinnamic acids gave the corresponding 3-benzylthioinden-1-ones; Dieckmann reactions with ethyl β-(benzylsulphonyl)cinnamates afforded the corresponding 2,5-diphenylthiophen-3(2*H*)-one 1,1-dioxides. Ethyl α-ethoxymethyl-*trans*-cinnamate is readily obtained from ethyl β-benzylsulphonyl-α-methyl-*cis*-cinnamate.

We have reviewed [1] methods for assigning configurations to β-(phenylthio)cinnamic acid derivatives from n.m.r. data. By use of these methods geometry was assigned to the β-benzylthio- and β-benzylsulphonyl-cinnamic acids and esters (I)—(IV) (see Table 1). The geometry of the α-substituted compounds (V)—(XII) was deduced from the position of the ester proton signals (see ref. 2). There is only a slight difference (*ca.* 0·09 p.p.m.) between the signals of the methylene protons in the sulphides (Ia) and (IIIa) and those in the corresponding sulphones (IIa) and (IVa). This contrasts with the larger shift (average 0·89 p.p.m.) in the resonance of the methylene protons which accompanies the change from $-S\cdot CH_2-$ into $-SO_2\cdot CH_2-$ in the other sulphide/sulphone pairs examined; the difference presumably is due to the presence of a *cis*-hydrogen atom in compounds (IIa) and (IVa) which may allow a conformation in which the methylene group receives a compensating shielding effect from the double bond. The methyl group resonance in the *cis*-compounds (Va)—(VIIIa) is at lower field than in the corresponding *trans*-isomers but there is only a small difference (*ca.* 0·1 p.p.m.) between the methyl resonances in the sulphides and those in the corresponding sulphones.

Cyclisation of either the *cis*- or *trans*-isomers of the β-benzylthiocinnamic acids (I), (V), and (IX) with phosphorus pentoxide gave the corresponding indenones (XIII)—(XV). Interconversion of the geometrical isomers of β-arylthiocinnamic acids occurs readily under acid-catalysis conditions (*cf.* ref. 3 and references therein). In the case of the *trans*-isomers of compounds (I), (V), and (IX) isomerisation and subsequent cyclisation to the indenone occurs rather than cyclisation to a seven-membered 2-benzothiepinone. The indenones (XIII) and (XIV) were also prepared by reactions of the corresponding indane-1,3-diones with toluenethiol. In each of these reactions the benzylthioindenone was accompanied by the corresponding thioacetal, 1,1,3-trisphenylthioindene and 2-methyl-1,1,3-trisphenylthioindene, respectively.



(XIII) R = H
(XIV) R = Me
(XV) R = Br



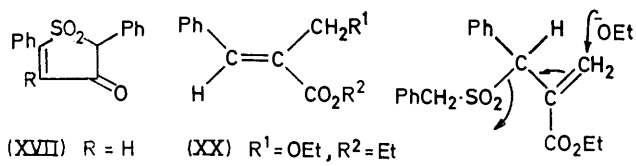
(XVI)

Whereas 2-methylindenone (XIV) was a stable compound, the 2-bromo-analogue (XV) slowly decomposed and the indenone (XIII) dimerised on dissolution in ether or chloroform. 2-Phenylinden-1-one has been reported [4] to dimerise rapidly to a truxone, and the n.m.r. data for the dimer of the indenone (XIII) are consistent with a truxone structure (XVI). We have reported [3] that 3,3-diphenylindan-1-one was obtained from 2-bromo-3-phenylthioinden-1-one or directly from α-bromo-β-phenylthiocinnamoyl chloride by treatment with benzene and aluminium chloride. As expected, benzene in presence of aluminium chloride also reacted

[1] K. Buggle, J. J. Delahunty, and E. M. Philbin, *Proc. Royal Irish Acad.*, 1971, **71***B*, 257.
[2] T. Hayashi, *J. Org. Chem.*, 1966, **31**, 3253.
[3] K. Buggle, J. J. Delahunty, E. M. Philbin, and N. D. Ryan, *J. Chem. Soc.* (*C*), 1971, 3168.
[4] B. W. Rockett and C. F. Hauser, *J. Org. Chem.*, 1964, **29**, 1394; R. de Fazi, *Gazzetta*, 1927, **57**, 551.

with β-benzylthio-α-bromocinnamoyl chloride to yield 3,3-diphenylindan-1-one.

Attempts to cyclise the ethyl β-(benzylthio)cinnamates to 3-hydroxythiophens with strong base were unsuccessful. However the sulphones (IV) and (XII) underwent Dieckmann cyclisation to the corresponding sulphones (XVII) and (XVIII), which were shown by their i.r. and n.m.r. spectra to exist in the keto-form. In the cyclisation of a mixture of the *cis*- and *trans*-isomers of ethyl β-benzylsulphonyl-α-methylcinnamate (VIII) with n-butyl-lithium the keto-sulphone (XIX) was accompanied by a minor product, for which



(XVII) R = H (XX) R^1 = OEt, R^2 = Et
(XVIII) R = Br (XXI) R^1 = OMe, R^2 = Me
(XIX) R = Me (XXII) $R^1 = C_4H_8NO$, R^2 = Et

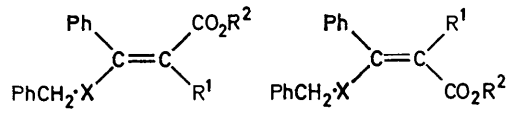
(A)

the structure (XX) was suggested by its n.m.r. spectrum and by the fact that its i.r. and u.v. spectra were similar to those of ethyl *trans*-cinnamate. Further evidence for the structure (XX) was afforded by ozonolysis and identification of the resulting benzaldehyde. Presumably ethyl α-ethoxymethyl-*trans*-cinnamate (XX) is formed by S_N2' attack by ethoxide ion (from the Dieckmann closure) on the tautomeric form (A) of the ester (VIII) (*cf.* ref. 5). Treatment of the *cis*-ester (VIIIa) with n-butyl-lithium yielded only starting material whereas under the same conditions the *trans*-ester (VIIIb) gave the Dieckmann product (XIX). When the ester (VIIIa) was treated with lithium ethoxide in ethanol the sole product was the compound (XX); methyl α-methoxymethyl-*trans*-cinnamate (XXI) was similarly formed by use of lithium in methanol. The conversion of the *cis*-sulphone (VIIIa) into the *N*-methylmorpholino-ester (XXII) was examined by n.m.r. spectroscopy. In [^{2}H]chloroform no detectable sulphone remained after 5 days; in [$^2H_4$]methanol conversion was complete in less than 24 h. The *trans*-sulphone (VIIIb) was also slowly converted into the morpholino-derivative (XXII) in [^{2}H]chloroform.

In connection with a project on addition reactions of 1,4-quinones the keto-sulphone (XVII) in ethanol was treated with 1,4-naphthoquinone to form the oxidised Michael adduct (XXIII). The less acidic keto-sulphone

TABLE 1

N.m.r. and i.r. spectral data for β-benzylthiocinnamic acids, esters, and sulphones



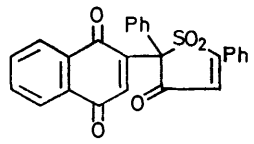
cis *trans*

	R^1	R^2	X	M.p. (b.p.) (°C)	Solvent	Configuration	ν_{CO}/cm^{-1}	τ =CH	τ =CMe	τ $-CH_2\cdot X-$	τ $-O\cdot CH_2$	τ Me
(Ia)	H	H	S	141—142	C_6H_6	*cis*	1680	4·14		5·96		
(Ib)	H	H	S	173—175 *	C_6H_6	*trans*	1665	4·02		6·31		
(IIa)	H	H	SO_2	154—155	C_6H_6	*cis*	1690	3·04		5·88		
(IIb)	H	H	SO_2	156—158	$CHCl_3$	*trans*	1695	3·35		5·45		
(IIIa)	H	Et	S	(185—190 at 1·5 mmHg)		*cis*	1720	4·06		5·96	5·96	8·92
(IIIb)	H	Et	S	(185—190 at 1·5 mmHg) *		*trans*	1698	4·03		6·28	5·71	8·68
(IVa)	H	Et	SO_2	118—120	C_6H_{12}	*cis*	1730	2·98		5·86	5·91	8·96
(IVb)	H	Et	SO_2	87—89	C_6H_{12}	*trans*	1730	3·48		5·59	5·68	8·68
(Va)	Me	H	S	133—134	C_6H_6	*cis*	1680		7·86	6·54		
(Vb)	Me	H	S	159—161	C_6H_6	*trans*	1660		8·25	6·57		
(VIa)	Me	H	SO_2	163—164	C_6H_6	*cis*	1700		7·77	5·80		
(VIb)	Me	H	SO_2	163—164	C_6H_6	*trans*	1738		8·03	5·60		
(VIIa)	Me	Et	S	(190—194 at 1·5 mmHg)		*cis*	1700		7·83	6·55	6·20	9·26
(VIIb)	Me	Et	S	(190—194 at 1·5 mmHg)		*trans*	1690		8·27	6·61	5·70	8·68
(VIIIa)	Me	Et	SO_2	84—85		*cis*	1720		7·66	5·80	6·13	9·21
(VIIIb)	Me	Et	SO_2	†		*trans*	1730		8·08	5·68	5·58	8·59
(IXa)	Br	H	S	148—150	C_6H_6	*cis*	1688			6·50		
(IXb)	Br	H	S	154—156 (decomp.)	C_6H_6	*trans*	1655			6·48		
(Xa) ‡	Br	H	SO_2	152—153	C_6H_6	*cis*	1715			5·37		
(XIa)	Br	Et	S	83—84		*cis*	1730			6·46	6·05	9·13
(XIb)	Br	Et	S	†		*trans*	1720			6·49	5·64	8·64
(XIIa)	Br	Et	SO_2	†		*cis*	1735			5·37	6·12	9·25
(XIIb)	Br	Et	SO_2	120—121	EtOH	*trans*	1740			5·62	5·52	8·58

* Ref. 6 gives m.p. 178° for (Ib) and b.p. 183—185° at 0·1 mmHg for (IIIb). † Colourless oil, purified by p.l.c ‡ The *trans*-isomer was not characterised.

[5] F. G. Bordwell, R. H. Hemwall, and D. A. Schexnayder, *J. Amer. Chem. Soc.*, 1968, **33**, 3233.

(XIX) did not add to 1,4-naphthoquinone under the same conditions.



(XXIII)

EXPERIMENTAL

N.m.r. spectra were recorded with a Perkin-Elmer R12 60 MHz spectrometer for solutions in [^{2}H]chloroform (unless otherwise stated) with tetramethylsilane as internal standard. I.r. spectra were determined with a Perkin-Elmer I.R. 700 spectrometer. Preparative layer chromatography (p.l.c.) was carried out on Merck Kieselgel PF 256 + 366.

β-(*Benzylthio*)*cinnamic Acids* (Ia *and* b).—A mixture of toluene-α-thiol (11·0 g) and ethyl benzoylacetate (9·0 g) containing zinc chloride (*ca.* 5·0 g; dried at 140°) was saturated with dry hydrogen chloride. After 2 h the solution was extracted with ether and the extract was washed successively with water, aqueous sodium carbonate (10%), and water, dried, and concentrated. The residual oil was taken up in ethanol. Partial evaporation yielded ββ-*bis*(*benzylthio*)*hydrocinnamate* as plates (14·0 g), m.p. 65—67° (Found: C, 70·7; H, 6·2; S, 15·1. $C_{25}H_{26}O_2S_2$ requires C, 71·1; H, 6·2; S, 15·2%), $\nu_{max.}$ 1730 cm^{-1}, τ 8·94 (3H, t, *J* 7·15 Hz), 6·74 (2H, s), 6·18 (2H, s), 6·11 (2H, s), 5·97 (2H, q, *J* 7·5 Hz), 2·5—2·7 (13H, m), and 2·0—2·2 (2H, m). A solution of the hydrocinnamate (5·0 g) in ethanol (100 ml) was added to a suspension of sodium hydroxide (3·0 g) in refluxing ethanol (150 ml) and the mixture was refluxed for 2 h. The alcohol was evaporated off and the residual paste was dissolved in water and acidified to pH 4 with hydrochloric acid (10%). The resulting precipitate on fractional crystallisation from benzene yielded (less soluble fraction) β-benzylthio-*trans*-cinnamic acid (Ib) (2·2 g), m.p. 173—175° (lit.,[6] 177°) and β-benzylthio-*cis*-cinnamic acid (Ia) (1·8 g), m.p. 141—142°.

TABLE 2

Analyses

	Formula	Found (%) C	H	Br	S	Required (%) C	H	Br	S
(Ia)	$C_{16}H_{14}O_2S$	71·0	5·5		12·0	71·1	5·2		11·8
(IIa)	$C_{16}H_{14}O_4S$	63·8	5·1		10·6	63·6	4·7		10·6
(IIb)	$C_{16}H_{14}O_4S$	63·6	4·7		10·8	63·6	4·7		10·8
(IIIa)	$C_{18}H_{18}O_2S$	72·1	6·0		11·3	72·5	6·1		10·7
(IVa)	$C_{18}H_{18}O_4S$	65·6	5·6			65·4	5·5		9·7
(IVb)	$C_{18}H_{18}O_4S$	65·8	5·5		9·8	65·4	5·5		9·7
(Va)	$C_{17}H_{16}O_2S$	72·0	5·2		11·5	71·8	5·7		11·3
(Vb)	$C_{17}H_{16}O_2S$	71·2	5·7		10·9	71·8	5·7		11·3
(VIa)	$C_{17}H_{16}O_4S$	64·2	5·0		10·3	64·6	5·1		10·1
(VIb)	$C_{17}H_{16}O_4S$	64·9	5·1		10·2	64·6	5·1		10·1
(VIIa)	$C_{19}H_{20}O_2S$	72·7	6·4		10·3	73·1	6·5		10·3
(VIIb)	$C_{19}H_{20}O_2S$	72·9	6·4		10·1	73·1	6·5		10·3
(VIIIa)	$C_{19}H_{20}O_4S$	66·3	5·7		9·4	66·3	5·9		9·3
(VIIIb)	$C_{19}H_{20}O_4S$	66·5	5·7		9·6	66·3	5·9		9·3
(IXa)	$C_{16}H_{13}BrO_2S$	55·5	3·8	23·0	9·3	55·0	3·7	22·9	9·2
(IXb)	$C_{16}H_{13}BrO_2S$	55·6	3·8	22·8	9·0	55·0	3·7	22·9	9·2
(Xa)	$C_{16}H_{13}BrO_4S$	49·8	3·7	21·3	8·3	50·4	3·4	21·0	8·4
(XIa)	$C_{16}H_{17}BrO_4S$	57·6	4·2	20·8	8·5	57·2	4·5	21·2	8·5
(XIb)	$C_{16}H_{17}BrO_4S$	57·1	4·3	21·0	8·3	57·2	4·5	21·2	8·5
(XIIa)	$C_{18}H_{17}BrO_4S$	52·2	4·2	19·9	7·8	52·8	4·2	19·5	7·8
(XIIb)	$C_{18}H_{17}BrO_4S$	52·7	3·9	19·5	8·0	52·8	4·2	19·5	7·8

β-*Benzylthio*-trans-*cinnamic Acid* (Ib).—A solution of phenylpropiolic acid (19·5 g) and sodium (3·45 g) in ethanol (100 ml; containing sufficient water to dissolve the sodium phenylpropiolate) at reflux temperature under nitrogen was treated with a solution of sodium (0·75 g) and toluene-α-thiol (18·6 g) in ethanol (50 ml). The solution was refluxed for 7 h. The alcohol was evaporated off and the residue on dissolution in water and acidification to pH 4 gave the *trans*-acid (Ib) (34·1 g).

β-(*Benzylsulphonyl*)*cinnamic Acids* (IIa *and* b), (VIa *and* b), *and* (Xa).—The appropriate β-benzylthiocinnamic acid (100 mg) in glacial acetic acid (2 ml) was treated with aqueous hydrogen peroxide (30%; 0·12 ml). The solution was heated on a steam-bath for 2 h, cooled, and poured into iced water. The precipitated β-(*benzylsulphonyl*)*cinnamic acid* (80—85%) was collected and crystallised.

Ethyl β-*Benzylsulphonylcinnamates* (IVa *and* b), (VIIIa *and* b), *and* (XIIa *and* b).—The *benzylsulphonyl-esters* (80—85%) were prepared from the corresponding benzylthio-esters by the method just described.

Ethyl β-(*Benzylthio*)*cinnamates* (IIIa *and* b).—The *ester* (IIIa) was prepared by esterification of the *cis*-acid (Ia) with diethyl sulphate and potassium carbonate in acetone. The *trans*-ester (IIIb) was prepared from ethyl phenylpropiolate and toluene-α-thiol as described previously.[6]

Ethyl β-*Benzylthio*-α-*methylcinnamates* (VIIa *and* b).—A mixture of ethyl α-benzoylpropionate (5·0 g) and toluene-α-thiol (6 ml) containing zinc chloride (*ca.* 2·5 g; dried at 140°) was saturated with dry hydrogen chloride. After 2 h the red solution was taken up in ether. The ether solution was washed successively with water, aqueous sodium carbonate (10%), and water, and then dried and concentrated. Distillation of the residual oil at 190—194° and 1·5 mmHg gave a mixture of the *cis*- and *trans*-isomers of ethyl β-benzylthio-α-methylcinnamate (3·8 g). P.l.c. (carbon tetrachloride chloroform) yielded (upper layer) the cis-*isomer* (VIIa) (2·1 g) and (lower layer) the trans-*isomer* (VIIb) (0·9 g).

β-*Benzylthio*-α-*methylcinnamic Acids* (Va *and* b).—The ethyl β-benzylthiocinnamates (VIIa and b) on saponification with ethanolic potassium hydroxide gave the corresponding *acids* (Va and b) in 85% yield.

Ethyl β-*Benzylthio*-α-*bromocinnamates* (XIa *and* b).—Bromine (4·8 g) in methylene chloride (15 ml) was added dropwise to a stirred solution of β-benzylthio-*trans*-cinnamic acid (8·1 g) in methylene chloride (40 ml) and the mixture was stirred for 20 min. The solvent was evaporated off and the residual solid taken up in acetone (40 ml) and refluxed for 2 h with potassium carbonate (5·0 g) and diethyl sulphate (5·1 g). Work-up with ether yielded a residue which was chromatographed (p.l.c.; carbon tetrachloride–chloroform) to give (upper band) the trans-*ester* (XIb) as a colourless liquid (0·75 g) and (lower band) the cis-*ester* (XIa) as a brown solid (4·9 g), m.p. (crude material) 82—83°, which decomposed on attempted recrystallisation.

β-*Benzylthio*-α-*bromocinnamic Acids* (IXa *and* b).—The α-*bromocinnamic acids* (IXa and b) were obtained (85%) by saponification of the ester (XIa and b), respectively.

Cyclisation of β-(*Benzylthio*)*cinnamic Acids.—General procedure.* Phosphorus pentoxide (75 mg) was added to a solution of the β-(benzylthio)cinnamic acid (100 mg) in benzene (10 ml). The mixture was refluxed, then filtered, and the inorganic residue was washed with hot benzene (3 × 15 ml). The combined benzene solutions were concentrated and the residual oil chromatographed (p.l.c.; carbon tetrachloride–chloroform).

(*a*) With a reaction time of 30 min and on half scale β-benzylthio-*trans*-cinnamic acid (Ia) gave (upper band)

[6] H. Scheibler and B. Frenz, *J. prakt. Chem.*, 1955, **2**, 127.

3-*benzylthioinden*-1-*one* (XIII) (65%), m.p. 116° (chloroform) (Found: C, 76·4; H, 5·0; S, 12·8. $C_{16}H_{12}OS$ requires C, 76·2; H, 4·8; S, 12·7%); $\nu_{max.}$ 1690 and 1600 cm^{-1}; τ 5·75 (2H, s), 4·21 (1H, s), and 2·62—2·9 (9H, m). The lower band was a mixture of the acid (Ia) and its isomer (Ib). Under similar conditions the *cis*-acid (Ib) also cyclised to the indenone (XIII) in 65% yield. When the cyclisation was carried out on a larger scale or for longer reaction times the yield of indenone was less.

(*b*) β-Benzylthio-α-methylcinnamic acid (Va) with a reaction time of 2 h gave (upper band) 3-*benzylthio*-2-*methylinden*-1-*one* (XIV) (65%), m.p. 110° (chloroform) (Found: C, 76·9; H, 5·3; S, 11·8. $C_{17}H_{14}OS$ requires C, 76·7; H, 5·2; S, 12·0%); $\nu_{max.}$ 1690 cm^{-1}; τ 8·11 (3H, s), 5·69 (2H, s), 2·74 (8H, s), and 2·0—2·15 (1H, m). The lower band was a mixture of acids (Va) and (Vb). The isomer (Vb) gave similar results.

(*c*) β-Benzylthio-α-bromocinnamic acid (IXa or b) with a reaction time of 2 h gave 3-*benzylthio*-2-*bromoinden*-1-*one* (XV) as a red-brown solid (75%), m.p. 78—80° (crude material) which slowly decomposed (Found: C, 58·1; H, 3·0; Br, 24·1; S, 9·5. $C_{16}H_{11}BrOS$ requires C, 58·0; H, 3·3; Br, 24·1; S, 9·7%); $\nu_{max.}$ 1705 cm^{-1}; τ 5·2 (2H, s) and 2·5—2·7 (9H, m).

Reaction of Toluene-α-thiol with Indane-1,3-*dione*.—Toluene-α-thiol (620 mg, 0·005 mol) was added slowly to a stirred solution of indane-1,3-dione (720 mg, 0·005 mol) in boron trifluoride–diethyl ether (25 ml), and stirring was continued for a further 5 h. The solution was poured into iced water and the ether solution separated. Work-up in the usual way gave an oil which was separated by chromatography (p.l.c.; carbon tetrachloride–chloroform) into three bands. The upper band contained dibenzyl disulphide (110 mg), the middle band 1,1,3-*trisbenzylthioindene* (170 mg), m.p. 94·5° (ethanol) (Found: C, 75·1; H, 5·5; S, 20·0. $C_{30}H_{26}S_3$ requires C, 74·7; H, 5·4; S, 19·9%); $\nu_{max.}$ 1530, 1490, and 1460 cm^{-1}; τ 6·43 (4H, s), 6·15 (2H, s), 4·33 (1H, s), and 2·7—2·8 (19H, m), and the lower band 3-benzylthioinden-1-one (XIII) (301 mg), m.p. 116°, identical with the sample obtained by cyclisation of the acids (I).

When the experiment was carried out with a three-molar excess of toluene-α-thiol, 1,1,3-trisbenzylthioindene was obtained in 65% yield.

Attempts to recrystallise 3-benzylthioinden-1-one from chloroform or ether led to the recovery of colourless *crystals*, m.p. 249° (chloroform) (Found: C, 76·2; H, 4·7; S, 12·3. $C_{32}H_{24}O_2S_2$ requires C, 76·2; H, 4·7; S, 12·7%); $\nu_{max.}$ 1720 cm^{-1}; τ($F_3C{\cdot}CO_2D$) 7·30 (2H, s), AB pattern (*J* 14 Hz), δ_A 6·65, δ_B 6·87 (3H), 3·4 (2H, m), 2·95 (6H, m), and 2·1 (m, 10H); τ($CHCl_3$) 7·32 (2H, s), 6·9 (AB pattern, 4H), and 2·0—3·4 (18H, m). The compound presumably has the truxone structure (XVI). The molecular ion was not apparent in the mass spectrum. The two most prominent peaks had *m/e* 412 (100%, $M - C_7H_8$) and 380 (38%, $M - PhCH_2{\cdot}SH$).

Reaction of Toluene-α-thiol with 2-*Methylindane*-1,3-*dione*.—2-Methylindane-1,3-dione (250 mg) on treatment with toluene-α-thiol (182 mg) in boron trifluoride–etherate as already described gave dibenzyl disulphide (18%), 1,1,3-*trisbenzylthio*-α-*methylindene* (15%), m.p. 90—92° (ethanol) (Found: C, 75·2; H, 5·9; S, 19·3. $C_{31}H_{26}S_3$ requires C, 75·0; H, 5·7; S, 19·3%); $\nu_{max.}$ 1590, 1490, and 1460 cm^{-1}; τ 8·07 (3H, s), 6·95 (4H, s), 6·04 (2H, s), and 2·85 (19H, m), and 3-*benzylthio*-2-*methylindenone* (XIV) (60%), m.p. 110° (chloroform) (Found: C, 76·9; H, 5·2; S, 11·8. $C_{17}H_{15}OS$ requires C, 76·7; H, 5·3; S, 12·0%); $\nu_{max.}$ 1690 cm^{-1}; τ 8·11 (3H, s), 5·68 (2H, s), and 2·7—2·9 (9H, m).

3,3-*Diphenylindan*-1-*one*.—A solution of β-benzylthio-α-bromo-*cis*-cinnamic acid (100 mg) in thionyl chloride (3 ml) was heated under reflux for 3 h. The thionyl chloride was distilled off and a suspension of aluminium chloride (65 mg) in benzene (10 ml) was added to the residue. The mixture was stirred for 30 min and poured on to iced water, and the whole was extracted with ether. The dried extract was concentrated and the residual oil chromatographed (p.l.c.; carbon tetrachloride–chloroform) to yield 3,3-diphenylindan-1-one (35 mg), m.p. and mixed m.p. 130—131° (lit.,[7] 130—131°).

2,5-*Diphenylthiophen*-3(2H)-*one* 1,1-*Dioxide* (XVII).—n-Butyl-lithium (30 mg) was added to a solution of ethyl β-benzylsulphonylcinnamate (a mixture of *cis*- and *trans*-isomers; 200 mg) in ether (20 ml), and the solution was stirred under nitrogen for 4 h. Water was added and the aqueous solution was separated, acidified with dilute hydrochloric acid, and extracted with ether. The ether solution yielded 2,5-*diphenylthiophen*-3(2H)-*one* 1,1-*dioxide* (XVII) (170 mg), m.p. 153—154° (ethanol) (Found: C, 68·1; H, 4·3; S, 11·3. $C_{16}H_{12}O_3S$ requires C, 67·7; H, 4·3; S, 11·3%); $\nu_{max.}$ 1705, 1590, and 1320 cm^{-1}; τ 4·94 (1H, s), 2·91 (1H, s), 2·48—2·7 (8H, m), and 1·9—2·1 (2H, m); pK_a (ethanol [8]) 4·43.

4-*Bromo*-2,5-*diphenylthiophen*-3(2H)-*one* 1,1-*Dioxide* (XVIII).—A mixture of the *cis*- and *trans*-isomers of ethyl β-benzylsulphonyl-α-bromocinnamate (60 mg) treated as just described gave the *bromo-sulphone* (XVIII) (42 mg), m.p. 145° (ethanol) (Found: C, 52·8; H, 3·2; Br, 22·1; S, 8·8. $C_{16}H_{11}BrO_3S$ requires C, 52·9; H, 3·05; Br, 22·0; S, 8·8%); $\nu_{max.}$ 1735, 1330, and 1278 cm^{-1}; τ 4·77 (1H, s), 2·25—2·75 (8H, m), and 1·8—2·0 (2H, m).

4-*Methyl*-2,5-*diphenylthiophen*-3(2H)-*one* 1,1-*Dioxide* (XIX).—Ethyl β-benzylsulphonyl-α-methyl-*trans*-cinnamate (50 mg), treated as just described, gave the *sulphone* (XIX) (39 mg), m.p. 152° (ethanol) (Found: C, 68·3; H, 4·8; S, 11·0. $C_{17}H_{14}O_3S$ requires C, 68·45; H, 4·7; S, 10·7%); $\nu_{max.}$ 1730, 1320, and 1170 cm^{-1}; τ 7·71 (3H, s), 4·98 (1H, s), and 2·25—2·75 (10H, m); pK_a [8] 4·72.

When a mixture (*ca.* 50%) of the *cis*- and *trans*-isomers of ethyl β-benzylsulphonyl-α-methylcinnamate (250 mg) was treated as just described the products were the keto-sulphone (XIX) (55 mg) and *ethyl* α-*ethoxymethyl*-trans-*cinnamate* (XX), an oil (60 mg) (Found: C, 71·8; H, 7·5. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%); $\nu_{C=O}$ 1700 and 1630 cm^{-1}; $\lambda_{max.}$ 269 nm (ε 14,600); τ 8·74 (3H, t, *J* 7·7 Hz), 8·63 (3H, t, *J* 7·0 Hz), 6·34 (2H, q, *J* 7·7 Hz), 5·64 (2H, q, *J* 7·0 Hz), 5·64 (2H, s), 2·5 (5H, m), and 1·99 (1H, s). Ozonolysis of the oil followed by treatment of the reaction mixture with lithium aluminium hydride and subsequent analysis by g.l.c. gave benzaldehyde.

Ethyl β-benzylsulphonyl-*cis*-cinnamate was unchanged when similarly treated.

Ethyl α-*Ethoxymethyl*-trans-*cinnamate* (XX).—Lithum ethoxide (16 mg) was added to a solution of ethyl β-benzylsulphonyl-*cis*-cinnamate (110 mg) in ethanol (5 ml) and the mixture was stirred overnight. Work-up with ether gave ethyl α-ethoxymethyl-*trans*-cinnamate (75 mg, 90%), identical with the material prepared before.

[7] C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, 1941, **6**, 516.

[8] W. Huber, ' Titrations in Non-aqueous Solvents,' Academic Press, New York, 1967, p. 140.

Methyl α-Methoxymethyl-trans-*cinnamate* (XXI).—Prepared by the reaction of lithium methoxide in methanol with ethyl β-benzylsulphonyl-*cis*-cinnamate, *compound* (XXI) was an oil (95%) (Found: C, 69·8; H, 7·0. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%); $\nu_{max.}$ 1710 and 1640 cm^{-1}; $\lambda_{max.}$ 269 nm (ε 15,850); τ 6·5 (3H, s), 6·09 (3H, s), 5·69 (2H, s), 2·5 (5H, m), and 1·94 (1H, s).

Ethyl α-(Morpholinomethyl)-trans-*cinnamate* (XXII).—Morpholine (25 mg) was added to a solution of the *cis*-ester (VIIIa) (68 mg) in [^{2}H]chloroform (0·25 ml) and the reaction was monitored by n.m.r. spectroscopy. After 48 h the ratio of the ester (VIIIa) to the product (XXII) was 50 : 50, after 74 h 33 : 66, and after 136 h only the product (XXII) was detectable. P.l.c. gave *ethyl α-(morpholinomethyl)*-trans-*cinnamate* (58 mg) as an oil (Found: C, 69·4; H, 7·8; N, 5·1. $C_{16}H_{21}NO_3$ requires C, 69·8; H, 7·7; N, 5·1%); $\nu_{max.}$ 1705 and 1610 cm^{-1}; $\lambda_{max.}$ 267 nm (ε 16,000); τ 8·12 (3H, t, *J* 7·8 Hz), 7·47 (4H, m), 6·58 (2H, s), 6·27 (4H, m), 5·65 (2H, q, *J* 7·8 Hz), 2·4 (5H, m), and 2·05 (1H, s).

When [$^2H_4$]methanol was the solvent the ratio of ester (VIIIa) to product was 40 : 60 after 6 h and after 24 h the reaction was complete.

Ethyl β-benzylsulphonyl-α-methyl-*trans*-cinnamate (VIIIb) similarly afforded the ester (XXII) on treatment with morpholine in deuteriochloroform.

Reaction of 2,5-*Diphenylthiophen*-3(2H)-*one* 1,1-*Dioxide with* 1,4-*Naphthoquinone*.—A solution of 1,4-naphthoquinone (158 mg) in ethanol (2 ml) was added to a solution of the keto-sulphone (XVII) (142 mg) in ethanol (5 ml). After 2 h the solvent was partially evaporated off and the adduct (XXIII) separated as *microcrystals* (150 mg), m.p. 214° (ethanol) (Found: C, 70·8; H, 3·9; S, 6·7. $C_{26}H_{16}O_5S$ requires C, 70·9; H, 3·7; S, 7·3%); $\nu_{max.}$ 1700 and 1650 cm^{-1}; $\lambda_{max.}$ 278 (ε 22,000) and 243 (32,000) nm; τ 2·96 (2H, s) and 2·25 (14H, m).

A similar reaction with 1,4-naphthoquinone and the sulphone (XIX) resulted in recovery of starting materials.

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