

288. *Mesomorphism and Chemical Constitution. Part VII.* The Effect of Halogen Substitution on the Mesomorphism of the trans-p-n-Alkoxy-cinnamic Acids.*

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The preparation and mesomorphic characteristics of certain *trans-4-n*-alkoxy-3-halogenocinnamic acids are described. The breadth and polarisation of the *trans-p-n*-alkoxycinnamic acids are increased by halogen substitution, and the effect of these changes is shown by the altered thermal stabilities of the mesophases. The presence of chlorine or bromine does not entirely eliminate the mesomorphic properties, although in the broader bromo-derivatives the long-chain dodecyl, hexadecyl, and octadecyl ethers alone exhibit mesophases, and these are monotropic. On the other hand all *trans-4-n*-alkoxy-3-iodocinnamic acids are non-mesomorphic. Such behaviour accords with that of the *trans-4-n*-alkoxy-3-halogenobenzoic acids.

THE changes in mesomorphic behaviour which accompany substitution in the 3-position of the *p-n*-alkoxybenzoic acids and in the 5-position of the 6-*n*-alkoxy-2-naphthoic acids have already been examined.^{1,2} In order to make further comparisons possible, a study has been made of the effect of halogen substitution on the mesomorphism of the *trans-p-n*-alkoxycinnamic acids.³ The m. p.s and mesomorphic transition temperatures (solid-smectic or -nematic, smectic-nematic, and smectic- or nematic-isotropic) of the 3-chloro-, 3-bromo-, and 3-iodo-derivatives are contained respectively in Tables 1, 2, and 3. In the chloro-series thirteen *n*-ethers (methyl—decyl, dodecyl, hexadecyl, and octadecyl) were prepared and examined, but since in the bromo-series mesomorphism does not occur until the dodecyl ether, and in the iodo-series no anisotropic phases are found, only a few of the lower ethers were prepared.

* Part VI, Gray, Hartley, Ibbotson, and Brynmor Jones, *J.*, 1955, 4359.

¹ Gray and Brynmor Jones, *J.*, 1954, 2556.

² *Idem*, *J.*, 1955, 236.

³ *Idem*, *J.*, 1954, 1467.

In the chloro-series, the hexyl ether is the first to exhibit mesomorphism and both the smectic and the nematic phase are monotropic. The lower m. p.s of the heptyl and octyl ether make possible enantiotropic nematic phases, but the smectic phases remain monotropic. The increasing stability of the smectic phase in the nonyl, decyl, and dodecyl

TABLE 1. *trans-4-n-Alkoxy-3-chlorocinnamic acids.*

Alkyl	Temp. of transition to			Alkyl	Temp. of transition to		
	smectic	nematic	isotropic		smectic	nematic	isotropic
Methyl	—	—	251°	Octyl	(127°)	130·5°	140°
Ethyl	—	—	206	Nonyl	125·5	131	138
Propyl	—	—	183·5	Decyl	122	133	137
Butyl	—	—	170	Dodecyl	116	133·5	134
Pentyl	—	—	159·5	Hexadecyl	115·5	—	129
Hexyl	(< 140·5°)	(144°)	148	Octadecyl	118·5	—	126·5
Heptyl	(120)	136·5	140·5				

TABLE 2. *trans-4-n-Alkoxy-3-bromocinnamic acids.*

Alkyl	Temp. of transition to isotropic	Alkyl	Temp. of transition to		
			smectic	nematic	isotropic
Methyl	250·5°	Nonyl	—	—	139·5°
Ethyl	214·5	Decyl	—	—	136·5
Hexyl	160·5	Dodecyl	(<127°)	(128°)	129
Heptyl	149	Hexadecyl	(122·5)	—	126
Octyl	142	Octadecyl	(121)	—	125

TABLE 3. *trans-4-n-Alkoxy-3-iodocinnamic acids.*

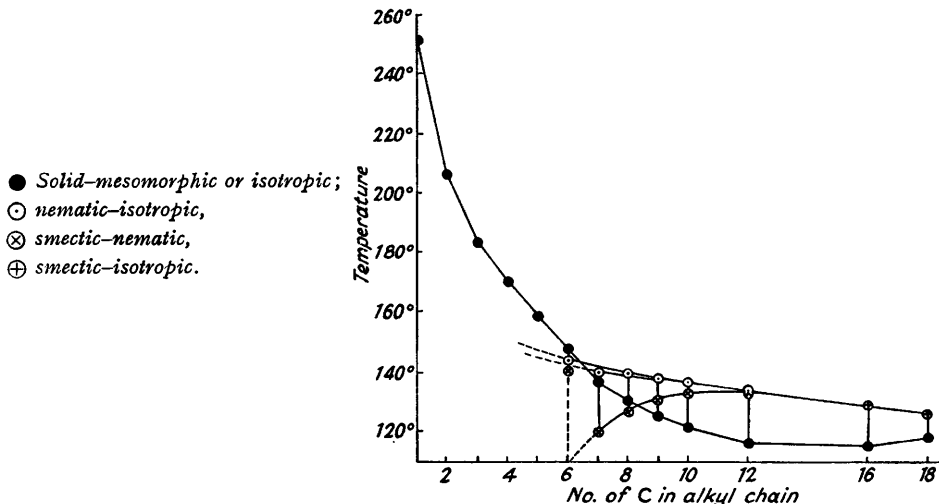
Alkyl	M. p.	Alkyl	M. p.	Alkyl	M. p.
Methyl	239·5°	Octyl	158°	Dodecyl	150·5°
Butyl	193	Nonyl	157·5	Hexadecyl	147·5
Hexyl	181	Decyl	156·5	Octadecyl	142
Heptyl	169				

ethers allows enantiotropic phases of both types. The hexadecyl and the octadecyl ether exhibit only smectic behaviour. When the m. p.s and mesomorphic transition temperatures for this series are plotted against the number of carbon atoms in the *n*-alkyl chain (see Figure), the points show the customary regularities found for homologous series of mesomorphic alkoxyarene-carboxylic acids. Thus, the smectic–nematic transition points for the heptyl–dodecyl ethers lie on a rising curve which reaches a maximum before joining the falling curve through the nematic– and smectic–isotropic points for the ethers containing even-carbon chains (hexyl–octadecyl). Only two ethers containing odd-carbon chains (heptyl and nonyl) give nematic–isotropic transition points, but these, as usual, lie slightly below the upper transition-point curve for even members of the series. These two points constitute what is probably the end of a similar smooth curve, which, if the isotropic melts of the lower ethers could supercool sufficiently, would pass through the “ monotropic nematic–isotropic points ” for the methyl, propyl, and pentyl ethers. The m. p. curve in this series is surprisingly regular and falls, steeply at first, to a minimum at the dodecyl ether, before rising to the m. p.s of the hexadecyl and the octadecyl ether. This curve, which is almost smooth, cuts the upper transition-point curve between hexyl and heptyl, and the smectic–nematic curve between octyl and nonyl, and so renders several of the phases monotropic. These are the figures in parentheses in Table 1. When the isotropic melt of the hexyl ether is cooled, the nematic phase first appears and the transition point is readily determined. Unless this phase is rapidly chilled, the smectic phase is not visible and crystallisation occurs at 140·5°. Consequently, the nematic–smectic transition point lies below this temperature, but it could not be determined. If, however, the smectic–nematic transition point curve (Figure) is extrapolated, the transition point for the hexyl ether is seen to be about 110°.

In the bromo-series, the dodecyl, hexadecyl, and octadecyl ethers alone exhibit mesophases. The isotropic melt of the dodecyl ether does not supercool greatly, and only the isotropic–nematic point could be determined. The hexadecyl and the octadecyl ether

show smectic phases, and in both cases these are monotropic. The upper transition points of these three ethers lie on a section of a curve, the whole of which would undoubtedly constitute a normal mesomorphic-isotropic transition-point curve if the lower members of the series were mesomorphic.

Mesomorphic-isotropic transition temperatures are available for the dodecyl, hexadecyl, and octadecyl ethers of the *p*-alkoxycinnamic acids,³ and their 3-chloro- and 3-bromo-derivatives. The mean of the three values may be taken in each case as an indication of



the average relative mesomorphic stability for this particular part of the series. These are summarised in Table 4, which also includes the changes in average transition temperature on passing from the unsubstituted acid to the substituted acid.

TABLE 4.

3-Substituent in the <i>p</i> -alkoxycinnamic acid	H	Cl	Br
Average mesomorphic-isotropic transition temperature (C ₁₃ —C ₁₈).....	160.5°	129.8°	123.8°
Decrease in transition temperature from unsubstituted acid		30.7°	36.7°

The introduction of the chlorine atom therefore decreases the mesomorphic transition temperature by 30.7°. This decrease in thermal stability must be the result of the two opposing effects of the chlorine substituent—first, the C-Cl dipole will increase the molecular polarisation and the mesomorphic thermal stability, and secondly, the increase in molecular breadth due to the chlorine atom will increase the molecular separation, weaken the intermolecular forces maintaining the molecular orientation in the mesophase, and decrease the thermal stability. The effect of bromine is only slightly greater than that of chlorine, and the decrease in average transition temperature from the unsubstituted acid is 36.7°—a result which accords with the fact that the C-Br dipole (1.71 μ) is not substantially different from the C-Cl dipole, and that the increase in breadth from chloro- to bromo-substituted cinnamic acid is only 0.27 Å. That is, the 6° thermal stability decrease from chloro- to bromo-series is the net result of these small changes in breadth and permanent polarisation, together with the different polarisability of the two molecule types.

Iodine as a substituent increases the molecular breadth more (1.83 Å), and the increase in permanent polarisation of the molecule (1.48 μ) is less than with chlorine and bromine. As a result, the 4-alkoxy-3-iodocinnamic acids show no mesomorphism.

The same general decrease in the mesomorphic thermal stability of the *p*-alkoxybenzoic acids has already been observed¹ when the molecular breadth is increased to such an extent that increased polarisation and polarisability fail to counteract the decrease in intermolecular cohesion. In this case the 4-alkoxy-3-fluoro- and 4-alkoxy-3-chlorobenzoic acids alone are mesomorphic. Considering once more the dodecyl—octadecyl

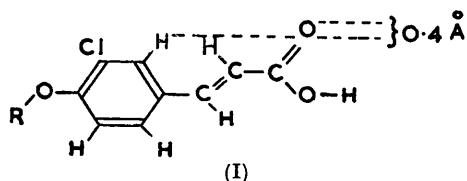
ethers, the average mesomorphic-isotropic transition temperatures, together with the corresponding decreases from unsubstituted to substituted acid, are given in Table 5.

TABLE 5.

3-Substituent in the 4-alkoxybenzoic acid	H	F	Cl
Average mesomorphic-isotropic transition temperature (C_{12} — C_{18}).....	133.5°	108.2°	84°
Decrease in transition temperature from unsubstituted acid		25.3°	49.5°

Here again an increase in substituent size decreases the mesomorphic stability, the fluorine atom (C—F dipole, 1.57 μ ; breadth increase 0.43 Å) by 25.3°, and the chlorine atom (C—Cl dipole, 1.73 μ ; breadth increase 1.18 Å) by 49.5°.

Chlorine has a greater effect in decreasing the average transition temperature of the benzoic acids than of the cinnamic acids, although it should alter the permanent polarisation and the polarisability of the two types to a similar degree. However, it must be



remembered that, although the benzenoid and the ethylenic part of a *trans-p-n*-alkoxy-cinnamic acid are no broader than for a *p*-alkoxybenzoic acid, the carboxyl group protrudes beyond the benzene and the ethylenic hydrogen atoms to a distance of about 0.4 Å. The molecule appears to be most symmetrical when the alkoxy-group, lying in the plane of

the ring, adopts a *trans*-configuration relative to the ethylenic linkage. Moreover, for steric reasons, the chlorine atom in the 3-position must be *trans* to the alkoxy-group. In consequence, the chlorine atom will probably lie on the side of the molecule on which the carboxyl group protrudes—an arrangement represented in (I).

A chlorine atom may therefore increase the breadth of the cinnamic acid molecule to a smaller extent (about 0.8 Å) than it will the benzoic acid molecule (1.18 Å), and consequently, its effect in reducing the mesomorphic thermal stability should be greater in the latter series. A similar result has been observed in the 6-alkoxy-5-chloro-2-naphthoic acids which are no broader than the unhalogenated acids.² In this case the chloro-derivatives have the higher mesomorphic transition temperatures. However, the 6-alkoxy-5-bromo-2-naphthoic acids, like the 4-alkoxy-3-bromo- and 4-alkoxy-3-chloro-cinnamic acids, are broader (0.22 Å) than the 5-chloro-acids. In both cases the bromine reduces the thermal stability compared with that of the chloro-derivatives, and it is interesting that the decreases (considering the C_{12} — C_{18} ethers in all cases) are very similar in each instance, 6° from chloro- to bromo-cinnamic acid, and 4.7° from chloro- to bromo-naphthoic acid.

No smectic-nematic transition temperatures are available for the 4-alkoxy-3-bromo-cinnamic acids, and, in considering the relative stability changes of the smectic phase, only the unsubstituted and 3-chloro-4-alkoxy-benzoic and -cinnamic acids need be considered. The average values for the nonyl, decyl, and dodecyl ethers are contained in Table 6.

TABLE 6.

3-Substituent	H	Cl	Decrease
Average smectic-nematic transition temperature (C_9 — C_{18}) for :			
(a) <i>p</i> -alkoxybenzoic acids	122.7°	89.8°	32.9°
(b) <i>p</i> -alkoxycinnamic acids	150.5	132.5	18

Here again, chlorine decreases the mesomorphic thermal stability, but to a smaller extent in the cinnamic acids.

It is in general true that, relatively to the unsubstituted acid, any one substituent decreases the thermal stability of the smectic phase to a smaller extent than that of the nematic phase. This arises through the increases in polarisability and permanent polarisation of the acid dimer caused by, for example, the introduction of the chlorine atom. In the smectic phase, the component of the C—Cl dipole which acts at right angles to the long axis of the molecule reinforces that in neighbouring molecules. Together with the decrease in lateral cohesions arising from the increased molecular separation, this effect will lead to a less marked reduction in thermal stability of the smectic phase than of the nematic phase, in which this dipole reinforcement does not occur.

The order of decreasing mesomorphic thermal stability for unsubstituted alkoxyarene-carboxylic acids has already been given³ as naphthoic > cinnamic > benzoic, and it is now seen that this sequence is also applicable to the substituted acids. The above order was originally related to the decreasing number of double bonds in the molecules, but is more accurately described in terms of the decreasing molecular polarisability as the number of C-H, C-C, and C=C bonds decreases. The marked stability of the phases of the 4'-*n*-alkoxydiphenyl-4-carboxylic acids, in which there are 12 carbon atoms and related bonds in the central nucleus, is a further illustration of this effect.⁴

The mesomorphic behaviour of these substituted cinnamic acids indicates that their configuration is *trans*. The *cis*-isomers would be considerably broader, and the molecular attractions would be much reduced.

EXPERIMENTAL

M. p.s are corrected.

Determination of Transition Temperatures.—The mesomorphic and polymorphic transition temperatures were determined in an electrically heated microscope block.⁵ The enantiotropic mesomorphic changes were measured in the usual way, and all values, except those involving solid-mesomorphic transitions, were checked by both heating and cooling the specimen. Like the *trans-p-n*-alkoxycinnamic acids,³ the 3-halogeno-derivatives tend to decompose on prolonged heating, so freshly mounted slides were used for each transition-point determination and exposure to high temperatures was minimised as far as possible. The procedure for determination of monotropic transition temperatures involving mesophases was as described for the 4-alkoxy-3-halogenobenzoic acids.¹ In these substituted cinnamic acids, the changes observed in polarised light were from the solid to the fine mosaic of smectic focal-conic groups, from the solid or the smectic phase to the mobile, threaded nematic phase (somewhat obscured by pseudomorphism in the 3-chloro-acids), and from the solid or the mesophase to the extinct isotropic liquid. In those members of both mesomorphic series which are purely smectic, characteristic bâtonnets are seen only when the isotropic liquid is cooled very slowly, and they very soon coalesce to give the fine mosaic of focal-conics.

Polymorphism occurs to a marked degree in the non-mesomorphic 4-alkoxy-3-iodocinnamic acids, and the solid-solid transition temperatures for this series are contained in the annexed table.

Alkyl	Transition temperature of Solid I-solid II	Alkyl	Transition temperature of	
			Solid I-solid II	Solid II-solid III
Octyl	157.5°	Dodecyl	113°	—
Nonyl	141	Hexadecyl	62.5	116.5°
Decyl	132	Octadecyl	87.5	123

Preparation of Materials.—The *p-n*-alkoxybenzaldehydes were prepared by homologous alkylation (methyl—decyl, dodecyl, hexadecyl, and octadecyl) of *p*-hydroxybenzaldehyde as described by Gray and Brynmor Jones.³

4-n-Alkoxy-3-chlorobenzaldehydes. The *p-n*-alkoxybenzaldehyde (0.1 mole) was dissolved in glacial acetic acid (50 ml.), and to the solution was added dichloramine-T (12 g., 0.05 mole) in glacial acetic acid (25 ml.). After the addition of concentrated hydrochloric acid (0.1 ml.), the mixture was refluxed for 6 hr., cooled, diluted, and extracted with ether. The extract was washed with water, dilute aqueous sodium hydroxide, and again with water, and dried and the ether was removed. The residual, crude *4-n-alkoxy-3-chlorobenzaldehydes* were distilled under reduced pressure and obtained as low-melting waxy solids. These products were very difficult to crystallise, and only one crystallisation from 90% ethanol was carried out. The solids give rather ill-defined m. p.s over a range of 2—4°, but give satisfactory results in the subsequent Knoevenagel condensation. The m. p.s and analyses are tabulated.

trans-4-n-Alkoxy-3-chlorocinnamic acids. The *p*-alkoxy-3-chlorobenzaldehyde (0.01 mole), malonic acid (1.6 g., 0.02 mole), pyridine (7 ml.), and piperidine (2 drops) were heated at 100° for 3 hr. The amount of pyridine was doubled in the case of the hexadecyloxy- and octadecyloxy-aldehyde. The precipitate obtained by pouring the mixture on ice (10 g.) and concentrated hydrochloric acid (10 ml.) was collected and washed with dilute hydrochloric acid and water. With the exception of the ethyl ether which was crystallised from benzene, the

⁴ Gray, Hartley, and Brynmor Jones, *J.*, 1955, 1412.

⁵ Gray, *Nature*, 1953, 172, 1137.

4-Alkoxy-3-chlorobenzaldehydes.

Alkyl	B. p./mm.	M. p.	Found (%)			Formula	Required (%)		
			C	H	Cl		C	H	Cl
Methyl *	128°/5	53°	56.5	4.1	20.8	C ₈ H ₇ O ₂ Cl	56.3	4.1	20.8
Ethyl	123°/5	64.5	58.6	4.9	19.1	C ₉ H ₉ O ₂ Cl	58.5	4.9	19.2
Propyl	118°/4	42	60.4	5.5	17.8	C ₁₀ H ₁₁ O ₂ Cl	60.5	5.6	17.8
Butyl	140°/3	27	62.2	6.2	16.6	C ₁₁ H ₁₃ O ₂ Cl	62.1	6.2	16.7
Pentyl	177°/9	32	63.5	6.7	15.7	C ₁₂ H ₁₅ O ₂ Cl	63.6	6.7	15.6
Hexyl	152°/4	30	64.9	7.0	14.7	C ₁₃ H ₁₇ O ₂ Cl	64.9	7.1	14.7
Heptyl	160°/4	34	66.1	7.4	14.1	C ₁₄ H ₁₉ O ₂ Cl	66.0	7.5	13.9
Octyl	151°/2	40	67.0	7.8	13.2	C ₁₅ H ₂₁ O ₂ Cl	67.0	7.9	13.2
Nonyl	189°/6	55	67.8	8.3	12.4	C ₁₆ H ₂₃ O ₂ Cl	67.9	8.2	12.5
Decyl	180°/2	54	68.8	8.5	11.9	C ₁₇ H ₂₅ O ₂ Cl	68.8	8.5	11.9
Dodecyl	189°/4	58.5	70.3	9.1	11.2	C ₁₉ H ₂₉ O ₂ Cl	70.2	9.0	10.9
Hexadecyl	216°/1	67.5	72.2	9.5	9.1	C ₂₃ H ₃₇ O ₂ Cl	72.5	9.8	9.3
Octadecyl	278°/2	71.5	73.1	9.8	8.9	C ₂₅ H ₄₁ O ₂ Cl	73.4	10.1	8.7

* Not new.

crude acids were crystallised from glacial acetic acid until the m. p.s were constant. After the first crystallisation the yields were about 70—90%, but about seven crystallisations were necessary to obtain samples satisfactory for transition-point determinations. The analyses are tabulated.

trans-4-Alkoxy-3-chlorocinnamic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	Cl		C	H	Cl
Methyl	56.4	4.3	16.7	C ₁₀ H ₉ O ₃ Cl	56.4	4.3	16.7
Ethyl	58.3	4.9	15.7	C ₁₁ H ₁₁ O ₃ Cl	58.3	4.9	15.7
Propyl	60.3	5.4	14.7	C ₁₂ H ₁₃ O ₃ Cl	59.9	5.4	14.8
Butyl	61.6	6.0	13.6	C ₁₃ H ₁₅ O ₃ Cl	61.3	6.0	13.9
Pentyl	62.7	6.6	13.0	C ₁₄ H ₁₇ O ₃ Cl	62.4	6.4	13.2
Hexyl	64.1	6.9	12.6	C ₁₅ H ₁₉ O ₃ Cl	63.7	6.8	12.6
Heptyl	64.8	7.3	11.7	C ₁₆ H ₂₁ O ₃ Cl	64.7	7.1	12.0
Octyl	65.9	7.4	11.4	C ₁₇ H ₂₃ O ₃ Cl	65.7	7.4	11.4
Nonyl	66.8	7.7	10.9	C ₁₈ H ₂₅ O ₃ Cl	66.7	7.8	10.9
Decyl	67.6	8.1	10.4	C ₁₉ H ₂₇ O ₃ Cl	67.6	8.1	10.5
Dodecyl	69.4	8.6	9.7	C ₂₁ H ₃₁ O ₃ Cl	69.1	8.6	9.7
Hexadecyl	71.4	9.3	8.3	C ₂₅ H ₃₉ O ₃ Cl	71.3	9.3	8.4
Octadecyl	72.1	9.7	7.9	C ₂₇ H ₄₃ O ₃ Cl	72.2	9.7	7.9

4-n-Alkoxy-3-bromobenzaldehydes. The *p*-alkoxybenzaldehyde (0.1 mole), in carbon tetrachloride (15 ml.) containing a trace of iodine, was refluxed with bromine (16 g., 0.1 mole), with constant stirring, until no more hydrogen bromide was evolved, and the solution was pale straw-coloured. The cooled solution was washed successively with aqueous sodium hypobromite, water, saturated aqueous sodium carbonate, and water. The solvent was then removed from the dried extract under reduced pressure, and the residual crude solids were crystallised from ethanol and light petroleum. The lower ethers were rather difficult to crystallise, and the yields after one crystallisation varied between 50 and 70%. The m. p.s and analyses are tabulated.

4-Alkoxy-3-bromobenzaldehydes.

Alkyl	M. p.	Found (%)			Formula	Required (%)		
		C	H	Br		C	H	Br
Methyl *	53°	44.5	3.6	37.4	C ₈ H ₇ O ₂ Br	44.7	3.3	37.2
Ethyl	60.5	47.2	4.1	34.8	C ₉ H ₉ O ₂ Br	47.2	4.0	34.9
Hexyl	47	54.6	6.0	28.0	C ₁₃ H ₁₇ O ₂ Br	54.7	6.0	28.0
Heptyl	51	56.2	6.4	26.7	C ₁₄ H ₁₉ O ₂ Br	56.2	6.4	26.7
Octyl	55	57.7	6.9	25.4	C ₁₅ H ₂₁ O ₂ Br	57.5	6.8	25.5
Nonyl	59.5	58.9	7.3	24.2	C ₁₆ H ₂₃ O ₂ Br	58.7	7.1	24.4
Decyl	59.5	59.9	7.7	23.7	C ₁₇ H ₂₅ O ₂ Br	59.8	7.4	23.4
Dodecyl	66.5	61.7	8.2	21.7	C ₁₉ H ₂₉ O ₂ Br	61.8	7.9	21.6
Hexadecyl	72	64.5	8.7	19.1	C ₂₃ H ₃₇ O ₂ Br	64.9	8.8	18.8
Octadecyl	82.5	66.2	9.3	17.7	C ₂₅ H ₄₁ O ₂ Br	66.2	9.1	17.6

* Not new.

trans-4-n-Alkoxy-3-bromocinnamic acids. These acids were prepared in the same way as the analogous chloro-derivatives. After one crystallisation from glacial acetic acid the yields

were 75—85%. The acids were then crystallised from acetic acid, benzene, and toluene until their m. p.s and transition temperatures were constant. The analyses are annexed.

4-Alkoxy-3-bromocinnamic acids.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	Br		C	H	Br
Methyl	46.7	3.7	31.1	C ₁₀ H ₉ O ₃ Br	46.7	3.5	31.1
Ethyl	48.9	4.4	29.6	C ₁₁ H ₁₁ O ₃ Br	48.7	4.1	29.5
Hexyl	55.4	6.2	24.3	C ₁₅ H ₁₉ O ₃ Br	55.1	5.8	24.5
Heptyl	56.4	6.4	23.2	C ₁₆ H ₂₁ O ₃ Br	56.3	6.2	23.5
Octyl	57.7	6.6	22.4	C ₁₇ H ₂₃ O ₃ Br	57.5	6.5	22.5
Nonyl	58.7	6.8	21.5	C ₁₈ H ₂₅ O ₃ Br	58.5	6.8	21.7
Decyl	59.7	7.0	20.8	C ₁₈ H ₂₇ O ₃ Br	59.5	7.0	20.9
Dodecyl	61.5	7.8	19.4	C ₂₁ H ₃₁ O ₃ Br	61.3	7.5	19.5
Hexadecyl	64.3	8.5	16.9	C ₂₅ H ₃₉ O ₃ Br	64.2	8.4	17.1
Octadecyl	65.4	8.7	16.2	C ₂₇ H ₄₃ O ₃ Br	65.5	8.7	16.2

4-Alkoxy-3-iodobenzaldehydes. The *p*-alkoxybenzaldehyde (0.05 mole) and iodine (16 g., 0.063 mole) were dissolved in ethanol (200 ml.). In the case of the hexadecyloxy- and octadecyloxy-aldehyde the volume of solvent was increased to 225 ml. Finely powdered mercuric oxide (16 g., 0.07 mole) was added, and the mixture vigorously stirred while concentrated sulphuric acid (5 ml., 94% w/w) was added dropwise during 15 min. Stirring was continued for 12 hr. at room temperature, whereupon the mixture was filtered. The filtrate was diluted with water (500 ml.) to precipitate the crude 4-alkoxy-3-iodobenzaldehydes, saturated aqueous sodium thiosulphate (250 ml.) was added, and the suspension thoroughly stirred. The iodo-compound was separated in nearly quantitative yield by filtration, except for the oily butyl ether which was extracted with chloroform and recovered after drying (Na₂SO₄). The impure products were then crystallised from light petroleum (b. p. 40—60°) until their m. p.s were constant.

4-Alkoxy-3-iodobenzaldehydes.

Alkyl	M. p.	Found (%)			Formula	Required (%)		
		C	H	I		C	H	I
Methyl	110.5°	36.6	2.4	48.7	C ₉ H ₇ O ₂ I	36.7	2.7	48.4
Butyl	22	43.5	4.4	41.7	C ₁₁ H ₁₃ O ₂ I	43.4	4.3	41.7
Hexyl	34.5	47.2	5.1	37.9	C ₁₃ H ₁₇ O ₂ I	47.0	5.2	37.9
Heptyl	37	48.7	5.6	36.5	C ₁₄ H ₁₉ O ₂ I	48.6	5.5	36.7
Octyl	44	50.0	5.9	35.0	C ₁₅ H ₂₁ O ₂ I	50.0	5.9	35.2
Nonyl	47.5	51.1	6.4	33.7	C ₁₆ H ₂₃ O ₂ I	51.3	6.2	33.9
Decyl	52	52.8	6.6	32.7	C ₁₇ H ₂₅ O ₂ I	52.6	6.5	32.7
Dodecyl	59.5	54.9	7.2	30.5	C ₁₉ H ₂₉ O ₂ I	54.8	7.0	30.5
Hexadecyl	75	58.6	7.9	26.7	C ₂₃ H ₃₇ O ₂ I	58.5	7.9	26.9
Octadecyl	76.5	59.8	8.4	25.3	C ₂₅ H ₄₁ O ₂ I	60.0	8.3	25.4

trans-4-n-Alkoxy-3-iodocinnamic acids. The acids were prepared in the manner described for the analogous chloro-derivatives. The amount of pyridine was increased to 14 ml. for the dodecyl, hexadecyl, and octadecyl ethers. The crude products were crystallised from glacial acetic acid (yield 90—95%), and then from benzene until constant m. p.s were obtained.

4-Alkoxy-3-iodocinnamic acids.

	Found (%)			Formula	Required (%)		
	C	H	I		C	H	I
Methyl	39.7	3.0	41.7	C ₁₀ H ₉ O ₃ I	39.5	3.0	41.7
Butyl	45.2	4.3	36.5	C ₁₃ H ₁₅ O ₃ I	45.1	4.4	36.7
Hexyl	48.2	5.3	33.7	C ₁₅ H ₁₉ O ₃ I	48.1	5.1	33.9
Heptyl	49.5	5.4	32.4	C ₁₆ H ₂₁ O ₃ I	49.5	5.5	32.7
Octyl	50.8	5.7	31.4	C ₁₇ H ₂₃ O ₃ I	50.8	5.8	31.6
Nonyl	51.9	6.0	30.4	C ₁₈ H ₂₅ O ₃ I	51.9	6.1	30.5
Decyl	52.9	6.2	29.4	C ₁₉ H ₂₇ O ₃ I	53.0	6.3	29.5
Dodecyl	55.3	6.8	27.5	C ₂₁ H ₃₁ O ₃ I	55.0	6.8	27.7
Hexadecyl	58.7	7.6	24.5	C ₂₅ H ₃₉ O ₃ I	58.4	7.6	24.7
Octadecyl	60.1	7.9	23.3	C ₂₇ H ₄₃ O ₃ I	59.8	8.0	23.4

Grants to the Department from the Distillers Company Limited and from Imperial Chemical Industries Limited are gratefully acknowledged.