Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Laterally Substituted 4-n-Alkylphenyl 4-n-Alkylbicyclo (2.2.2) octane-1-carboxylates

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Version of record first published: 14 Oct 2011.

To cite this article: G. W. Gray & S. M. Kelly (1981): Laterally Substituted 4-n-Alkylphenyl 4-n-Alkylbicyclo (2.2.2) octane-1-carboxylates, Molecular Crystals and Liquid Crystals, 75:1, 109-119

To link to this article: http://dx.doi.org/10.1080/00268948108073607

Mol. Cryst. Liq. Cryst., 1981, Vol. 75, pp. 109–119
0026-8941/81/7504-0109 $06.50/0

Printed in the United States of America

Laterally Substituted 4-*n*-Alkylphenyl 4-*n*-Alkylbicyclo(2.2.2)octane-1-carboxylates

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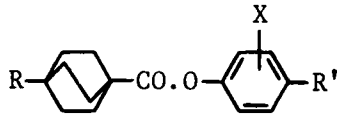
(*Received February 16, 1981*)

Different substituents (fluoro, chloro, bromo, and cyano) have been separately introduced into the 2-position of the phenolic moiety of the 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates to produce new series of low melting esters with large nematic ranges. In particular, thirty 4-*n*-alkyl-2-fluorophenyl and thirteen 4-*n*-alkyl-2-chlorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates are reported. The effect of the various lateral substituents on the clearing points and viscosities of the esters are rationalized in terms of steric interactions and the "shielding" properties of the bulky 1,4-disubstituted bicyclo(2.2.2)octane ring. Mixtures of the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates and cyanobiphenyls have useful electro-optical properties and have very low injected smectic tendencies.

INTRODUCTION

The high clearing points of the 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates[1,2] offer the possibility of incorporating various lateral substituents (X) into the 2- or 3-position of the phenolic moiety and thereby producing new series of esters (I) still having reasonably high clearing points, but modified physical properties, e.g., dielectric anisotropy, viscosity, etc. It was hoped that a suitable choice of lateral substituents would allow the already



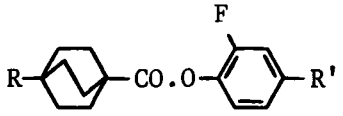
(I)

useful physical properties[2,3] of the 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)-octane-1-carboxylates to be altered advantageously with respect to certain re-

quirements of electro-optical displays. Also, by using different halogeno substituents in the esters, the relationships between substituent size, clearing point (T_{N-I}), and other physical parameters could be monitored in a systematic way.

RESULTS AND DISCUSSION

Thirty 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (II) have been prepared and the liquid crystal transition temperatures of these esters are recorded in Table I.



(II)

A typical plot of the liquid crystal temperatures of these fluoro-substituted bicyclo-octane esters (II) against the number of carbon atoms in the terminal alkyl chain of the phenolic moiety is depicted (for R, *n*-C_7H_{15}) in Figure 1. The trends shown in this figure are typical of many of the other series. The melting points generally decrease with increasing alkyl chain length, but in some cases the upper clearing point (T_{N-I}) curve may be slightly convex, such that the transition lines still rise at the longest chain lengths studied (R', *n*-C_8H_{17}).

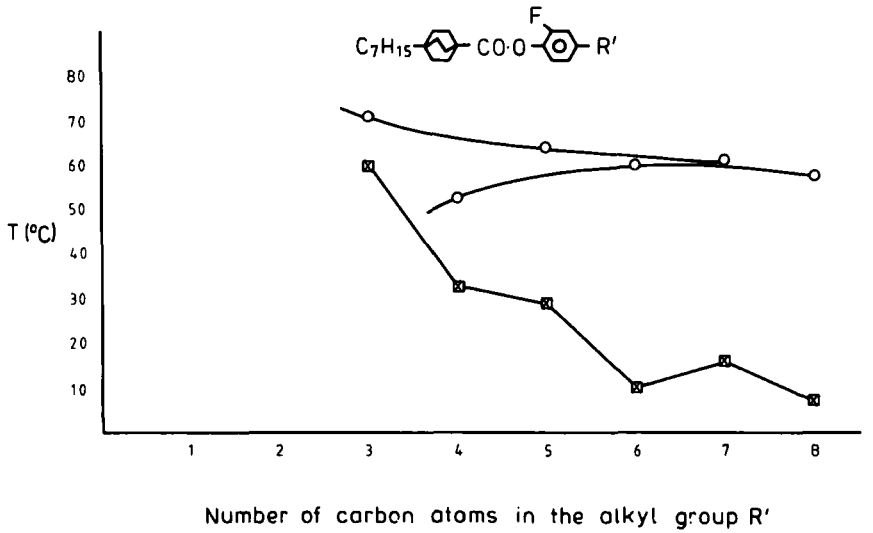
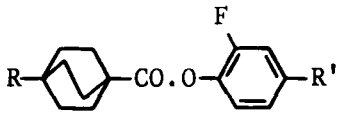


FIGURE 1 Plot of the transition temperatures against number of carbons in the alkyl chain R' of the esters formulated: O, nematic-isotropic liquid transition; ⊠, crystal-nematic transition.

TABLE I

Data for esters of structure



(II)

n-R	*n*-R′	Transition temperatures (°C) C—N/I	N—I
C_3H_7	C_3H_7	76	(58.5)
C_3H_7	C_4H_9	37	43
C_3H_7	C_5H_{11}	42	54.5
C_3H_7	C_6H_{13}	48	(45.5)
C_3H_7	C_7H_{15}	52	(51.5)
C_3H_7	C_8H_{17}	34	47.5
C_4H_9	C_3H_7	59	(46)
C_4H_9	C_4H_9	17	32.5
C_4H_9	C_5H_{11}	23	46.5
C_4H_9	C_6H_{13}	27	40
C_4H_9	C_7H_{15}	30	49
C_4H_9	C_8H_{17}	10.5	44
C_5H_{11}	C_3H_7	66.5	67
C_5H_{11}	C_4H_9	27.5	48.5
C_5H_{11}	C_5H_{11}	26	65
C_5H_{11}	C_6H_{13}	20[a]	55.5
C_5H_{11}	C_7H_{15}	11[b]	62.5
C_5H_{11}	C_8H_{17}	8.5	59
C_6H_{13}	C_3H_7	38	57
C_6H_{13}	C_4H_9	30	46
C_6H_{13}	C_5H_{11}	13[c]	48.5
C_6H_{13}	C_6H_{13}	10[d]	47.5
C_6H_{13}	C_7H_{15}	17[e]	54
C_6H_{13}	C_8H_{17}	16	50.5
C_7H_{15}	C_3H_7	60	71
C_7H_{15}	C_4H_9	33	53
C_7H_{15}	C_5H_{11}	29	64
C_7H_{15}	C_6H_{13}	10	60
C_7H_{15}	C_7H_{15}	16	61
C_7H_{15}	C_8H_{17}	7	58

( ) Denotes a monotropic transition temperature

[a] ΔH, 44.2 kJ mol^{-1}

[b] ΔH, 29.3 kJ mol^{-1}

[c] ΔH, 20.6 kJ mol^{-1}

[d] ΔH, 30.7 kJ mol^{-1}

[e] ΔH, 49.9 kJ mol^{-1}

Many of the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (II) exhibit very low melting points. Of the thirty esters prepared, eleven exhibit enantiotropic nematic phases at room temperature (C—N, $< 20°$), and twenty-two possess melting points lower than those of the analogous 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates.[1,2] Smectic phases have not been observed for any of the homologues studied and even esters with two long terminal alkyl chains (e.g., R, *n*-C_7H_{15}; R′, *n*-C_8H_{17}) are purely nematic, see Table I.

The average effect of the 2-fluoro-substituent on the T_{N-I} value of the analogous unsubstituted ester is remarkably small, and indeed in several individual cases the T_{N-I} value is *increased.* Over the range of esters examined the average decrease in clearing point is small ($-3°$) and the actual changes vary within fairly narrow limits ($-9° \leftrightarrow +2.5°$). The average decrease ($-3°$) in clearing point on incorporating this lateral substituent into this position of the dialkyl bicyclo-octane esters[1,2] is much smaller than the corresponding decreases observed for similar substitution of the related dialkyl cyclohexanoate esters ($-11°$)[4] or dialkyl benzoate esters ($-28°$).[4]

A number of factors may contribute to this situation, but the following considerations may, perhaps, predominate. If the 2-fluoro-substituent projects in the opposite direction to the carbonyl function of the ester group, it may then lie in the same plane, but this would cause a considerable broadening of the parent, unsubstituted ester. However, steric interactions between the fluoro-substituent and the oxygen of the carbonyl function may prohibit their lying next to each other in the same plane. If however the aromatic ring bearing the 2-fluoro-substituent takes up a position such that the fluoro-substituent projects upwards from the plane of the ester function, an intermediate situation may arise such that the intramolecular and intermolecular steric interactions and the rotational molecular diameter are all minimized. Such an intermediate conformational situation is shown in Figure 2.

If ring X is a benzene ring, then the thickness of the molecule may be considerably increased by introduction of the 2-fluoro-substituent. However, if ring X is the spherically symmetrical bicyclo(2.2.2)octane ring, then the broadening effect of the substituent may be marginal. When ring X is the non-planar cyclohexane ring, an intermediate increase may arise. The bulky 1,4-disubstituted bicyclo(2.2.2)octane ring is therefore presumed to "shield" the

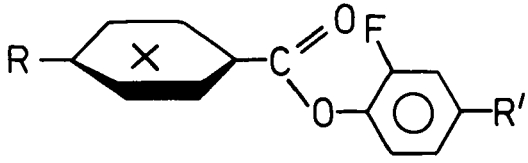
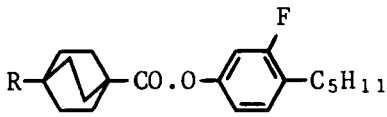


FIGURE 2 Illustration of a non-planar conformation of a fluoro-substituted ester (II).

2-fluoro-substituent to a large degree and thus minimize the intermolecular steric effects of the substituent. The *trans*-1,4-disubstituted cyclohexane ring thus appears to have a smaller, but still significant "shielding" effect.

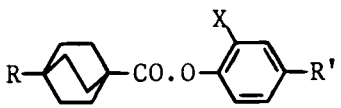
A fluoro-substituent was also introduced into the 3-position of the phenolic moiety of the esters to produce several 3-fluoro-4-pentylphenyl 4-*n*-alkylbicyclo-(2.2.2)octane-1-carboxylates (III). In three out of the four cases studied, incorporation of the fluorine into this position led to an *increase* in melting point, and in all four cases the clearing points (T_{N-I}) were markedly decreased by comparison with the parent unsubstituted esters. The liquid crystal transition temperatures of one member (R, *n*-C_5H_{11}) of this series exemplify these general results. The ester has a higher melting point (C—I, 44.5°) and a lower



(III)

clearing point (N—I, 38.5°) than either the corresponding unsubstituted dialkyl bicyclo-octane ester (C—N, 31°; N—I, 64.5°) or the 2-fluoro-substituted dialkyl bicyclo-octane ester (C—N, 26°; N—I, 65°). Considering these results, further esters incorporating substituents in this position in the phenolic part of the ester were not prepared. Presumably, in this more exposed position, the fluorine is not "shielded" by the bicyclo-octane ring and the full intermolecular steric effect of the substituent is felt.

The high clearing points of the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo-(2.2.2)octane-1-carboxylates (II) and the "shielding" effect of the bicyclo-octane ring presented us with the opportunity of introducing larger substituents into the 2-position of the phenolic moiety and thereby producing new series of esters which might still have moderately high clearing points. To this end, three new types of ester ((IV); X, Cl, Br, CN) were prepared and the liquid



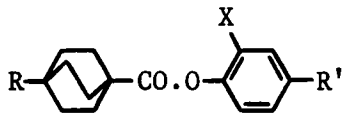
(IV)

crystal transition temperatures of these materials are recorded in Table II.

It is evident that introduction of even the bulky chloro- and cyano-substituents does not destroy the liquid crystal properties. Relatively small and fairly constant decreases in clearing point (average (Cl) ΔT_{N-I}, 26.5°; average (CN) ΔT_{N-I}, 31.5°) are observed for the incorporation of these substituents in this position, and several homologues (e.g., $5^{Cl}/7$, $5^{Cl}/8$, etc.) of the 4-*n*-alkyl-2-chlorophenyl series ((IV), X = Cl) exhibit quite wide-range enantiotropic

TABLE II

Data for esters of structure



(IV)

X	*n*-R	*n*-R'	Transition temperatures (°C) C—N/I	N—I	$\Delta T_{N-I}(H \rightarrow X)$
Cl	C_3H_7	C_5H_{11}	32	(29.5)	26
Cl	C_4H_9	C_5H_{11}	30	(19.5)	29.5
Cl	C_4H_9	C_6H_{13}	27	(14.5)	28.5
Cl	C_4H_9	C_7H_{15}	22[a]	25.5	26.5
Cl	C_4H_9	C_8H_{17}	14	22	28.5
Cl	C_5H_{11}	C_5H_{11}	35.5	41	23.5
Cl	C_5H_{11}	C_6H_{13}	30	(25)	33.5
Cl	C_5H_{11}	C_7H_{15}	17	40.5	24.5
Cl	C_5H_{11}	C_8H_{17}	13	35	27.5
Cl	C_6H_{13}	C_5H_{11}	25	36	18.5
Cl	C_6H_{13}	C_6H_{13}	20	28	26
Cl	C_6H_{13}	C_7H_{15}	35.5[b]	37.5	19.5
Cl	C_6H_{13}	C_8H_{17}	27.5	35.5	24
Br	C_5H_{11}	C_5H_{11}	14.5	27	37.5
CN	C_5H_{11}	C_5H_{11}	27.5	29.5	35
CN	C_6H_{13}	C_5H_{11}	26	26.5	28

( ) Denotes a monotropic transition temperature
[a] ΔH, 17.3 kJ mol^{-1}
[b] ΔH, 35.0 kJ mol^{-1}

nematic phases (23.5° and 22° respectively). Smectic phases have not been observed for any of the homologues studied despite substantial "supercooling" below the melting points for many of these esters (to −20°).

It can be seen that as the size of the lateral substituent is increased above the critical value of fluorine, the more substantial are the decreases in clearing point recorded. It is supposed that the relatively small fluoro-substituent can be approximately accomodated within the normal rotation volume of the parent dialkyl substituted bicyclo-octane ester with a marginal increase in the width of the molecule, i.e., the fluorine is almost totally "shielded" by the bulky bicyclo-octane ring. However, substituents larger than fluorine will substantially increase the molecular width of the resultant ester, with a consequent decrease in clearing point. It is clear that the larger the substituent, the greater the molecular broadening effect will be, and the greater is the resultant

decrease in clearing point. The effect on T_{N-I} is approximately linear in substituent size for the three substituents with a greater effective radius than fluorine.

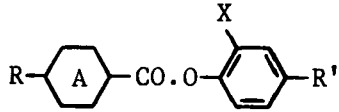
PHYSICAL PROPERTIES

The physical properties and electro-optical characteristics of the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (II) have been reported in detail[3] by colleagues at R.S.R.E. (Malvern). However, it is useful to summarize the major results in the present context.

The viscosity of the di-*n*-pentyl homologue ($5^F/5$) of the fluoro-substituted bicyclo-octane esters is moderately low (44 cSt at 20°C) compared with that of a binary mixture (3/5 and 5/5) of the corresponding 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (34 cSt at 20°C). The birefringence of the esters is low (0.075 for $5^F/5$) and high voltage mixtures of the fluoro-substituted esters with cyanobiphenyls (40% w/w) exhibit similar electro-optical responses to those of analogous mixtures using the parent, unsubstituted dialkyl bicyclo-octane esters, i.e., the sharpness is good (1.74), the temperature dependence of threshold voltage is low (0.37% C^{-1}), and the multiplexing margin is good (1:3; 10%). Moreover, the tendency of mixtures of the fluoro-substituted esters with cyanobiphenyls to give injected smectic phases is very small indeed.[7]

The viscosity of a binary mixture of two homologues ($3^{Cl}/5$ and $5^{Cl}/5$) of the 4-*n*-alkyl-2-chlorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates ((IV); X = Cl) is however high (ca 100 cSt at 20°C). Thus the electro-optical properties of the chloro-substituted bicyclo-octane esters are presumed to be markedly inferior to those of the corresponding unsubstituted and fluoro-substituted bicyclo-octane esters. This sudden and large increase in viscosity on passing from a fluoro- to a chloro-substituted bicyclo-octane ester is further evidence for the breakdown in the shielding effect of the bicyclo-octane ring with substituents of a greater size than fluorine. The birefringence of the chloro-substituted esters is again low (0.055 at 20°C).

Miscibility studies involving 4-cyano-4′-*n*-octylbiphenyl (C—S_A, 21.5°; S_A—N, 33.5°; N—I, 40.5°) and a given homologue selected from each of the



(V)

series of esters of general structure (V) yield the following order of decreasing

injection of mono-layer smectic A phases

A = benzene[4]		A = cyclohexane[4]		A = bicyclo-octane[1,2]		A = bicyclo-octane[7]
	>		>		≫	
X = H		X = H		X = H		X = F

The capacity of the 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (II) to suppress strongly the injection of smectic phases into the nematic mixtures is of obvious advantage for several display device applications. This property, combined with the high clearing points of the fluoro-substituted dialkyl bicyclo-octane esters (II) (average (F) T_{N-I}, 60°C) and their moderate viscosities render them superior to the corresponding fluoro-substituted dialkyl cyclohexanoates[4] (average (F) T_{N-I}, 40°C) and the fluoro-substituted dialkyl benzoates[4] (average (F) T_{N-I}, 10°C). In this context, the dielectric properties of the dialkyl bicyclo-octane esters are of course modified by the 2-substituent, the effect being most pronounced with the 2-cyano derivatives, e.g., $5^{CN}/5$; $\Delta\epsilon$, -2 (at $0.95 \times T_{N-I}$).

CONCLUSION

The 4-*n*-alkyl-2-fluorophenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates exhibit enantiotropic, wide-range nematic phases, often at room temperature. The introduction of the 2-fluoro-substituent incurs very little penalty in terms of T_{N-I}, due to the "shielding" effect of the bicyclo-octane ring. This effect only breaks down with larger 2-substituents, but the chloro-, bromo-, and cyano-analogues are still capable of forming enantiotropic nematic phases with reduced T_{N-I} values.

The physical properties of these 2-substituted esters are of interest. All the nematic phases are of low birefringence, and for the 2-fluoro esters the viscosity of the nematic phases is moderately low. This latter property combines well with good electro-optical properties to make the fluoro-substituted esters of considerable commercial interest.

EXPERIMENTAL

Transition temperatures

The liquid crystal transition temperatures recorded in Tables I and II were determined by optical microscopy using either a Vickers M72c polarizing microscope or a Nikon L-Ke polarizing microscope in conjunction with a Mettler FP52 heating stage and an FP5 control unit. The Mettler stage could be cooled ($< -20°$) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage. In those instances when it was not possible to observe a

liquid crystal transition directly, "virtual" nematic-isotropic liquid (N—I) transition temperatures were determined in the normal manner.

Spectral analysis

^{1}H nmr, infra-red, and mass spectra were determined using, respectively, a Jeol JNM-4H 100 Mz spectrometer, a Perkin Elmer 457 spectrometer, and an AEI MS 902 mass spectrometer.

Differential thermal analysis

Enthalpies of fusion for the most stable crystal forms of several of the esters ((II) and (IV); X = Cl) were measured using a Stanton Redcroft (Model 671) low temperature differential thermal analyzer (DTA). Indium was used as a standard for calibration, and the degree of error for the quoted enthalpy values is estimated at ±10%.

Birefringence

Birefringence was determined from the refractive indices for the homeotropically aligned nematic phase measured using an Abbé refractometer (Model 60/HR, wavelength 5896 nm).

Viscosity

Measurements of viscosity were made using two viscometers (types CMSM; sizes 200 and 350) supplied by Poulton, Lee and Selfe Limited. The viscometers had been calibrated, and the constants C at 25° were found to be 0.1160 and 0.5124 cSt s^{-1}.

Preparation of materials

The esters ((II) and (IV); X = Cl) were prepared by the interaction of the acid chlorides of the known 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acids[1] with the appropriate phenols, according to a literature method.[1] The necessary 4-*n*-alkyl-2-fluorophenols and 3-fluoro-4-pentylphenol were supplied by BDH Chemicals Limited (Poole), Dorset under a Ministry of Defense Supply Contract. The necessary 4-*n*-alkyl-2-chlorophenols, 2-bromo-4-pentylphenol, and 2-cyano-4-pentylphenol were prepared according to adapted literature methods.

Experimental details

2-Chloro-4-pentanoylanisole. A solution of pentanoyl chloride (12.7 g, 0.105 mol) and 2-chloroanisole (15 g, 0.105 mol) in sieve-dried dichloromethane (30 cm^3) was added dropwise to a mixture of anhydrous aluminum chloride (12.6 g, 0.095 mol) and sieve-dried dichloromethane (30 cm^3) cooled using an ice-

bath. The mixture was stirred overnight and allowed to attain room temperature. The solution was added to a small volume of 15% hydrochloric acid and stirred for 20 min. The organic layer was separated off and the aqueous layer shaken with chloroform (2×30 cm^3). The combined organic layers were washed with water (2×250 cm^3) and dried. After crystallization from methanol, the *2-chloro-4-pentanoylanisole* (16.5 g, 69%) had mp 58–59°; m/e, 226, 228.

Results for other homologues were: *hexanoyl,* m/e, 240, 242, 75%, mp 40–41°; *heptanoyl,* m/e, 254, 256, 82%, mp 24°; *octanoyl,* m/e, 268, 270, 82%, bp 180° at 0.5 mm Hg.

2-Bromo-4-pentanoylanisole was prepared similarly from 2-bromoanisole: m/e, 270, 272, 43%, mp 56–57°.

2-Chloro-4-pentylanisole. A solution of 2-chloro-4-pentanoylanisole (16 g, 0.071 mol) in sieve-dried chloroform (100 cm^3) was added dropwise to a stirred solution of aluminum lithium hydride (4.6 g, 0.117 mol) and anhydrous aluminum chloride (35.2 g, 0.265 mol) in sodium-dried ether (100 cm^3). The resultant mixture was heated under reflux overnight. After decomposition of the complex and excess of $LiAlH_4$, the organic layer was separated off and the aqueous layer was shaken with ether (2×80 cm^3). The combined organic layers were washed with brine (2×500 cm^3) and dried. After filtration, distillation of the crude product under reduced pressure yielded *2-chloro-4-pentylanisole* (13.0 g, 86.6%), bp 160° at 11.0 mm Hg; m/e, 212, 214.

Results for the other homologues were: *hexyl,* m/e, 226, 228 64% bp 166–170° at 21 mm Hg; *heptyl,* m/e, 240, 242, 67%, bp 184° at 21 mm Hg; *octyl,* m/e, 254, 256, 63%, bp 190–191° at 18.5 mm Hg.

2-Bromo-4-pentylanisole was prepared similarly from the bromo-ketone: m/e, 256, 258, 68%, bp 180–182° at 21 mm Hg.

2-Chloro-4-pentylphenol. A solution of 2-chloro-4-pentylanisole (13.0 g, 0.068 mol), hydrobromic acid in glacial acetic acid (80 cm^3), and 48–50% hydrobromic acid (50 cm^3) was heated under reflux for 18 h. The cooled reaction solution was added to water (200 cm^3), and the mixture shaken with ether (3×80 cm^3). The combined organic layers were washed with brine (2×500 cm^3) and dried. Distillation of the crude product under reduced pressure yielded *2-chloro-4-pentylphenol,* bp 154° at 22 mm Hg; m/e, 198, 200 (8.5 g, 70%).

Results for the other homologues were: *hexyl,* m/e, 212, 214, 73%, bp 130° at 1.0 mm Hg; *heptyl,* m/e, 226, 228, 67%, bp 120° at 0.4 mm Hg; *octyl,* m/e, 240, 242, 75%, bp 141° at 1.0 mm Hg.

2-Bromo-4-pentylphenol was prepared similarly from the corresponding ether: m/e, 242, 244 (39%), bp 152–153° at 0.2 mm Hg.

2-Cyano-4-pentylphenol. A solution of 2-bromo-4-pentylphenol (3.5 g, 0.0014 mol), copper (I) cyanide (0.3 g, 0.0035 mol) and sieve-dried 1-methyl-2-pyrrolidone (10 cm^3) was heated at a temperature of 200° for 3 h. The cooled reaction mixture was added to a solution of anhydrous iron (III) chloride (3.5 g) and concentrated hydrochloric acid (1 cm^3) in water (35 cm^3) and stirred at 50–60° for 20 min. This mixture was shaken with ether (3 × 80 cm^3) and the combined organic layers were washed with brine (2 × 250 cm^3) and dried. The crude 2-cyano-4-pentylphenol was distilled and yielded 1.1 g (40%), bp 170–172° at 1.0 mm Hg; m/e, 189.

Acknowledgments

This paper is published by permission of the Director HMSO and the authors thank the UK Ministry of Defense for a research grant. The authors also thank BDH Chemicals Limited (Poole), for the supply of the appropriate 4-*n*-alkyl-2-fluorophenols and 3-fluoro-4-pentylphenol, colleagues at R.S.R.E. (Malvern) for permission to publish electro-optical data recorded in this publication, and Miss T. Srithanratana for the use of her results on injected S_A properties of mixtures.

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