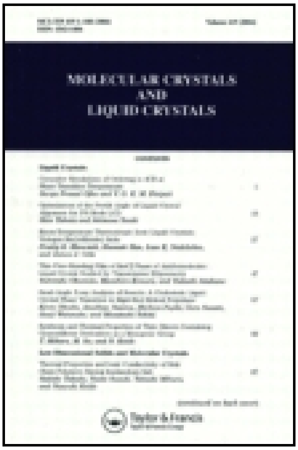

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The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates. 4. Phenylbenzoates Containing A $(CH_2)_nCO_2R^{l}$Group (n = 0-2) on the Phenolic End

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The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates. 4. Phenylbenzoates Containing A $(CH_2)_nCO_2R'$Group (n = 0–2) on the Phenolic End†

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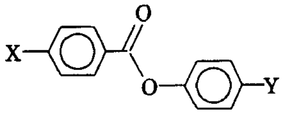

The effect of a $(CH_2)_nCO_2R'$ group on the mesomorphic properties of the esters where X= alkyl or alkoxy, $Y=(CH_2)_nCO_2R'(R'=C_7$ and $C_9)$ and n = 0–2 has been studied by synthesizing these esters and determining their mesomorphic properties by hot-stage polarizing microscopy. The starting phenols were prepared by esterification of hydroxy protected 4-hydroxybenzoic, phenylacetic or phenylpropionic acids. Both the benzyl and methoxycarbonyl protecting groups were tried with the latter giving higher yields when n = 0 because of better solubility of the protected acid. No mesophases were observed in the esters when n = 1, nematic and smectic A phases occurred when n = 2 and smectic A and C phases when n = 0. A few 1,4-cyclohexane diesters were also prepared using these phenols. The mesomorphic properties of these esters followed the same trend observed in the phenylbenzoates except no C phases were observed.

Comparisons of the transition temperatures for these esters with those for Y=R′ showed that both small increases or decreases were observed for $Y=CO_2R'$. However, the addition of a spacer methylene group (n = 1 and 2) always gave lower temperatures with the amount of lowering being much greater for n = 2 than n = 1. A comparison of transition temperatures for $Y=CO_2R'$, OCOR′, COR′ and OR′ indicated that these temperatures were highest when Y=COR′ as expected from dipole moment considerations but were lower when $Y=CO_2R'$ than when Y=OCOR′; the opposite expected from these considerations. This trend was also observed in the cyclohexane diesters. Transition temperatures were always higher for the esters when Y has an oxygen atom adjacent to the benzene ring. Therefore, esters with $Y=O(CH_2)_nCO_2R'$, n = 1 and 2 were also synthesized. The phenols were prepared by alkylation of 4-benzyloxyphenol with the bromo esters followed by hydrogenolysis. However, these esters showed no mesophases except the cyclohexane diester with n = 2.

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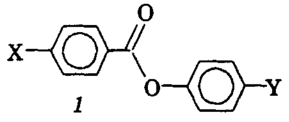
INTRODUCTION

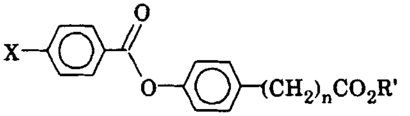
A comparison of the effect on mesomorphic properties of replacing the alkyl chain on the phenolic end of the phenylbenzoates *1a* with an α-keto chain *1b*[1] with that of substituting an acyloxy group *1c* for an alkoxy group *1d*[2] indicates that the α-keto group affects a greater change on the transition temperatures than does the acyloxy group (Figure 1).



1

	Y
a	R'
b	COR'
c	OCOR'
d	OR'

Since the terminal ester group can be attached to the benzene ring either through the ether oxygen atom as in *1c* or via the carbonyl carbon atom, we were also interested in determining the effect of the carboxylate group in the esters *2* on mesomorphic properties.



	n
2	0
3	1
4	2

If only dipole moments are considered (Table I), the effect on the carboxylate group on transition temperatures should be between that of the acyloxy and keto groups. When the keto and carboxyl groups are attached directly to the benzene ring, their dipoles are enhanced by conjugation and their rotation restricted by this conjugation with the aromatic ring. Thus, they could be considered part of the core of the molecule rather than the chain. We were also interested in determining the effect on mesomorphic properties of adding spacer methylene groups to the ester chains in the esters *3* and *4* by removing the polar carbonyl containing group away from the benzene ring where it would no longer be part of the core and freer to rotate. In polymers, the introduction of ester groups into aliphatic chains, even when they are attached to benzene rings give polymers with lower melting temperatures than those without ester groups.[5,6] The increased freedom of rotation around the CO—O bond which leads to more gauche conformers was offered as the explanation for this result. Apparently, this effect is strong enough to override the increased intermolecular interactions due to the added dipole. It was also found that the closer the ester group is to the center of the chain, the greater the decrease in melting temperatures.

Another structure factor to consider is the effect of steric hindrance to packing on mesomorphic properties. Among the branched chain phenylbenzoates, a methyl group on an alkyl chain close to the benzene ring usually lowers transition temperatures.[7,8] Although this could be due to steric hindrance to packing as originally proposed, it could also be due to the presence of more gauche conformers. Among the carbonyl containing chains, the carboxylate group should have less steric hindrance with the benzene ortho protons than does the acyloxy group. Thus, higher

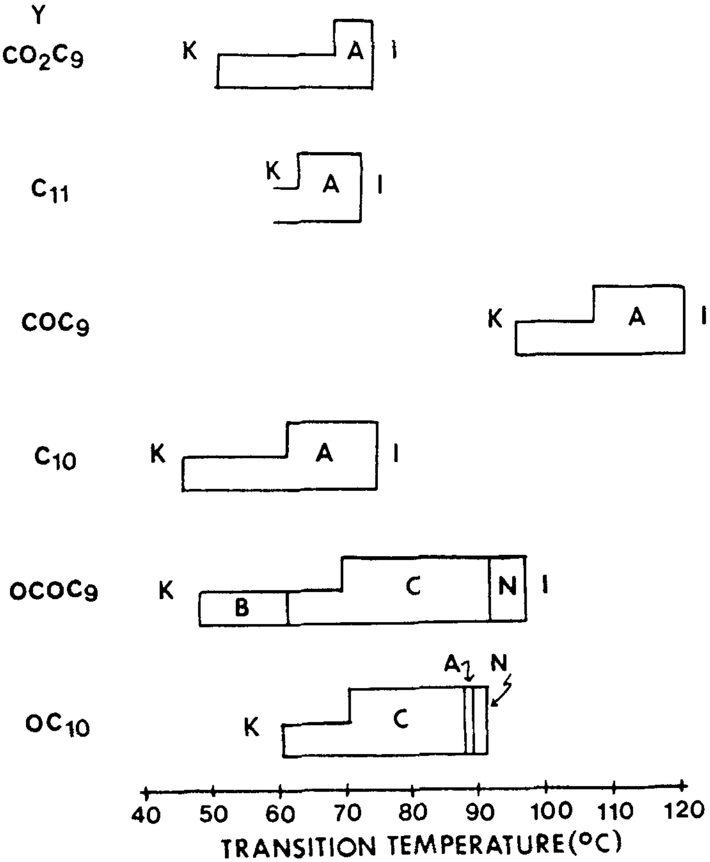
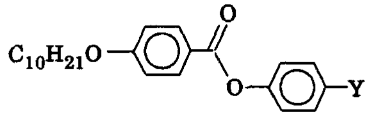


FIGURE 1 Mesomorphic Properties for



Data for Y=COC_9 from Reference 1, $OCOC_9$ from Reference 2, C_{10} and OC_{10} from Reference 3, and Y=C_{11} are predicted values.

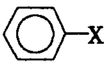
transition temperatures and better mesophases would be expected for this group than observed for the acyloxy group.

To test these ideas, we prepared a few homologs of the esters *2–4* with X=R,RO and R′=C_7 and C_9. Several of the corresponding cyclohexane diesters *5–7* were also synthesized, as in our earlier work, to test the generality of our results.

	n
5	0
6	1
7	2

TABLE I

A Comparison of Dipole Moments for

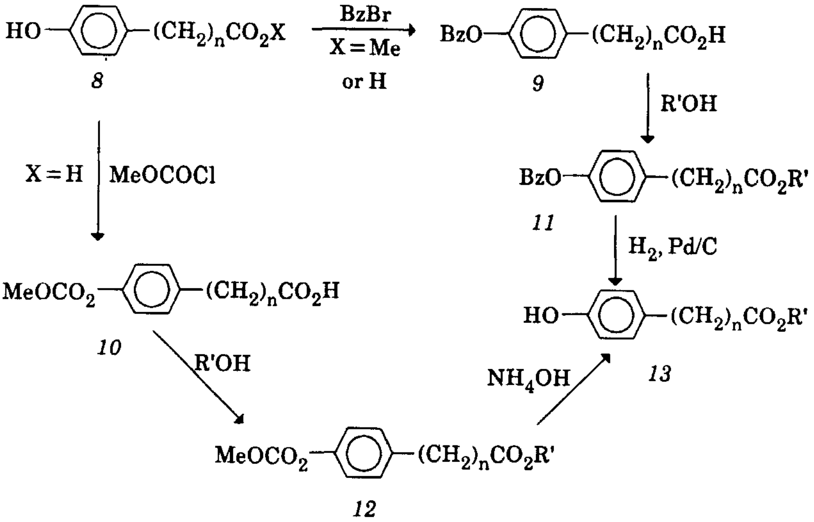


X	μ(D)[a]
Me	0.37
OMe	1.28
OCOMe	1.69
CO_2Me	1.83
CO_2Et	1.9
COMe	2.96

a. Data from ref. 4.

SYNTHESIS

The preparation of these esters required the synthesis of three phenols *13* (Scheme 1). Initially, an attempt was made to protect the phenolic hydroxy group with a benzyl group as we had done previously in the synthesis of alkoxy phenols.[9] However, the acid *9* with $n = 0$ was difficult to esterify due to its low solubility in organic solvents. Neither the usual carbodiimide or acid chloride methods[2] or even the acid chloride in pyridine method gave satisfactory results. Our best result was obtained using *p*-TSA and pyridine in the carbodiimide procedure but the purified



SCHEME 1

yield of the ester was only 36.4%. Better yields (41.0–67.8%) were obtained when spacer groups were added to the chain increasing the solubility of the acids. Use of the methoxycarbonyl group to protect the phenol using the method of Chin and Goodby[10] gave more soluble protected acids in all three cases with resulting higher yields throughout the synthesis (Scheme 1): 70.0–88.0% (blocking), 75.0–91.9% (esterification) and 66.7–86.7% (deblocking). This method, however, has the disadvantage that the intermediates were liquids which had to be purified by flash chromatography or by vacuum distillation rather than by recrystallization.* Structures of the phenols *13* and their precursors were confirmed by IR and NMR.

The phenylbenzoates *2–4* were prepared by esterification of these phenols with the appropriate acid using either the carbodiimide or acid chloride methods as described earlier.[2] The cyclohexane diesters *5–7* could not be prepared using the acid chloride method as previously described[12] since trace amounts of phosphoryl chloride hydrolyzed the chain ester causing esterification of the alcohol produced with the cyclohexane diacid chloride. The desired esters *5–7* were prepared using the carbodiimide method. All esters were purified by recrystallization from absolute ethanol and flash chromatography until they showed only one spot by TLC. IR and NMR spectra were used to confirm their structures; typical examples of NMR data (spectra for R/RO phenylbenzoates given in Reference 13 were used to help identify peaks) and experimental procedures are given in the experimental section.

In our continuing work preparing a variety of the phenylbenzoates with terminal chains containing ester groups, we have often observed broad clearing temperatures in these esters even though they appeared to be pure materials as we first mentioned in Reference 14. We have now discovered among the esters *2–7* that these broad clearing temperatures do indeed indicate the presence of small amounts (~3–4%) of impurities (with similar R_f or t_R values) as shown by HPLC on silica gel. We have usually been able to remove these impurities by flash chromatography as described in the experimental section. Sharp clearing temperatures were then observed although there was little difference in the temperatures.

MESOMORPHIC PROPERTIES

Mesomorphic properties for the phenylbenzoates *2–4* determined by hot stage polarizing microscopy are given in Table II and for the cyclohexane diesters *5–7* in Table III. Abbreviations are given in the experimental section.

Comparisons of transition temperatures of the phenylbenzoates with those for the analogous straight chain alkyl esters were made difficult by the problem of choosing the appropriate chain length alkyl esters to use as standards. Ideally, the terminal chain backbone should include the same number of atoms, both carbon and oxygen for the esters *1a* and *2–4*. Initially, we prepared the chain lengths we felt would give the most number of mesophases without regard to known alkoxyalkyl esters which could be used as standards. Thus, data for some of the necessary

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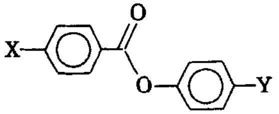
* Recently, use of an acetyl group to protect the OH group was reported. See Reference 11. A referee suggested using the NaOH/DMF-benzene alkylation method reported in Reference 9.

TABLE II

Transition Temperatures (°C) for



X	Y	K	C	A	N	I
C_5	CO_2C_9	41.2				52.0-53.7
C_{10}	CO_2C_9	64.8				68.5-69.8
C_6O	CO_2C_7	19.6		48.2-48.7		65.4-66.2
	CO_2C_9	27.1		51.3-51.4		62.3-62.6
$C_{10}O$	CO_2C_7	47.8		63.5-64.7		75.0-75.2
	CO_2C_9	51.5		66.8-69.4[a]		74.4-74.7
$C_{12}O$	CO_2C_7	59.5	(60.6)	72.4-72.8		76.7-76.8
	CO_2C_9	65.9	(66.8)	74.0-75.4		75.8-75.9
C_{10}	$CH_2CO_2C_9$	35.3[b]				54.2-55.4
C_6O		40.0				47.2-49.4
$C_{10}O$		47.0				50.7-52.4
C_{10}	$(CH_2)_2CO_2C_7$	18.6				24.3-26.9
C_6O		-7.5			(11.5-11.8)	26.3-27.6
C_8O		13.4		(21.7-21.8)	(25.4-25.8)	26.3-28.7
$C_{10}O$		23.6		(32.3-32.5)		35.6-36.2
C_8O	$(CH_2)_2CO_2C_9$	-16.6				39.6-41.3
$C_{10}O$		26.9		(34.5-34.8)	---	41.9-42.6
$C_{12}O$		35.6		(40.8-41.2)	---	45.6-48.7
C_6O	$OCH_2CO_2C_8$	40.6[c]				53.8-56.0
$C_{10}O$		62.3				67.5-68.2
$C_{10}O$	$O(CH_2)_2CO_2C_8$	61.8				70.3-70.8

a. Heating and cooling DSC scans confirmed the presence of only one mesophase: $\Delta H = 2.05$ kcal/mole (melting) and 9.59 kcal/mole (clearing).

b. At least 2-3 crystalline phases were observed depending on the cooling conditions. One crystalline form melted at 40.6-44.2 to insure that only one crystalline form was present at a time. The crystallized sample was allowed to set at RT for 24 hr and then heated at 2°/min. This showed a K_2-K_1 transition at 48.7-50.8°.

c. K_2-K_1 at 42.1-52.0° on heating.

standards were not available limiting the number of comparisons that can be accurately made. However, studies of the transition temperatures for all known straight chain alkyl/alkoxyphenylbenzoates indicate that predictions of transition temperatures for esters for which data are not available in the region of medium

TABLE III

Transition Temperatures (°C) for

Y	K	B	A	N	I
CH_3O_2C					162.5[a]
EtO_2C	146.0			153.4-155.7	193.4-194.0[b]
C_7O_2C	49.6[c]		68.4-69.1	---	143.9-144.2
C_9O_2C	67.8		79.8-80.7	---	138.0-138.3
$C_9O_2CCH_2$	71.9				88.7-89.3
$C_4O_2C(CH_2)_2$	56.4			(56.8-57.1)[d]	64.8-66.5
$C_7O_2C(CH_2)_2$	46.8	60.1-61.1			76.0-76.9
$C_9O_2C(CH_2)_2$	50.8	58.4-59.1			68.4-68.9
$C_{12}O_2C(CH_2)_2$	65.4				70.3-71.5
$C_8O_2CCH_2O$	97.3				98.1-99.8
$C_8O_2C(CH_2)_2O$	75.4			78.4-79.4	90.9

a. Data from reference 15.

b. Sample available at LCI but source is unknown.

c. This crystal form converted to a second one on cooling 2°/min at 49.5°.

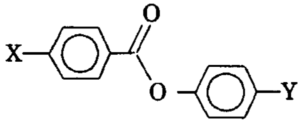
d. Observance of this phase depends on crystallization temperature.

to long chains are fairly accurate since these temperatures vary little between homologs.[16] Thus, we used predicted values for those homologs for standards for which data were not available for comparisons in transition temperatures. These comparisons are presented in Tables IV and V. The differences in melting temperatures when Y=CO_2R' compared to Y= an alkyl chain varied between positive and negative values whereas the clearing temperatures were usually only a little higher. The presence of one spacer group gave lower melting temperatures but no mesophases whereas two spacer groups lowered both the melting and clearing temperatures considerably and gave monotropic N and A phases.

A better comparison can be made between the transition temperatures for the esters with Y=CO_2R' and OCOR′ (Table VI). Usually the melting temperatures for Y=CO_2R' were lower than for Y=OCOR′; the opposite of what we would predict. Clearing temperatures were lowered even more. When the transition temperatures for the esters with X=$C_{10}O$ and Y=OCOR′, CO_2R' and COR′ in order of increasing dipole moment are compared (Figure 1), the α-keto group which has

TABLE IV

Comparison of Melting Temperatures for Carbonyl Containing Chains versus Alkyl Ones in



X	Y=R	$Y=CO_2R'$		$Y=CH_2CO_2R'$		$Y=(CH_2)_2CO_2R'$	
	R^a	R'	Diff	R'	Diff	R'	Diff
C_6O	C_9	C_7	10.2				
	C_{11}[b]	C_9	~-2.1			C_7	~-28.0
	C_{12}[c]			C_9	-11.4		
C_8O	C_{11}[b]					C_7	~-26.3
$C_{10}O$	C_9	C_7	-3.3				
	C_{11}[b]	C_9	~5.9			C_7	~-27.3
	C_{12}			C_9	-12.8		
	C_{13}[b]					C_9	-24.4
$C_{12}O$	C_{11}	C_9	~1.9				
	C_{13}[b]					C_9	~-26.3

a. **Values for known esters were obtained from our data base of transition temperatures for these esters (see ref. 3).**

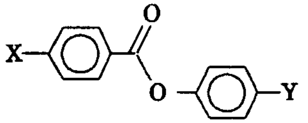
b. **Predicted transition temperatures were used for this ester.**

c. **New data for $X=C_6O$, $Y=C_{12}$: 60.4-61.2 (K-N), 62.1-62.2 (N-I), (51.3-51.4) (A-N), and 39.8 (A-K).**

the largest dipole moment also has the highest transition temperatures as expected, but the CO_2R' group, with a slightly larger dipole moment than the OCOR′ group, has the lowest clearing temperature and a melting temperature the same as that for the OCOR′ group. Additionally, the carbonyl containing group with the smallest dipole moment, OCOR′, gives the most mesophases. A comparison of the transition temperatures for the cyclohexane diesters (Table VII) with chains containing carbonyl groups indicate that both melting and clearing temperatures are substantially lower in the $Y=CO_2R'$ series than in the other 2 series. Interestingly these temperatures are highest when Y=OCOR′ rather than COR′. Again, esters with Y=OCOR′ have the most mesophases. Longer chain homologs of these esters have C phases and it is possible this would also be true when $Y=CO_2R'$. The effect of adding spacer groups to the CO_2R' chain in the cyclohexane diesters, *6* and *7* (Table III) on transition temperatures was the same as in the phenylbenzoates; temperatures were lowered when $n = 1$ and 2 and no mesophases were observed when $n = 1$. However, the mesophase combinations differed in that only nematic

TABLE V

Comparison of Clearing Temperatures (°C) for Carbonyl Containing Chains versus Alkyl Ones for



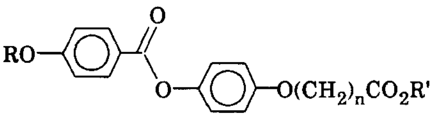
X	Y=R	Y=CO_2R'		Y=$(CH_2)_2CO_2R'$	
	Ra	R'	Diff	R'	Diff
C_6O	C_9	C_7	+1.3		
	C_{11}[a]	C_9	~-2.5	C_7	~-53.3
C_8O	C_{11}[a]			C_7	~-43.4
$C_{10}O$	C_9	C_7	2.2		
	C_{10}				
	C_{11}[a]	C_9	~1.7	C_7	~-40.5
	C_{13}[a]			C_9	-33.7
$C_{12}O$	C_{11}	C_9	~0.4	C_9	~-22.8

a. Predicted transition temperatures were used for this ester.

b. Values for known esters were obtained from our data base of transition temperatures for these esters (see ref. 3).

and smectic B phases were observed when $n = 2$. Unlike the phenylbenzoates, no smectic C phases were found.

Since only two types of mesophases (smectic A and N) were observed in the phenylbenzoates with Y=$(CH_2)_nCO_2R'$ whereas two additional phases occur in the esters with Y=OCOR', it seemed reasonable that insertion of an oxygen atom between the spacer and the benzene ring in the esters *14* would increase the smectic polymorphism.

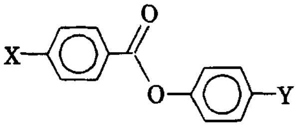


14a n=1
14b n=2

Therefore, we prepared the phenols *16* as shown in Scheme 2. Alkylation of 4-benzyloxyphenol with the ester bromide *15* with $n = 1$ was done using our anhydrous NaOH/DMF-benzene method described earlier,[9] but the Na_2CO_3/acetone method was used to prepare the diether *17* with $n = 2$ to avoid elimination. Surprisingly, the phenylbenzoates prepared from these phenols showed no mesophases (Table II) although a N phase was observed in the cyclohexane diesters *19*

TABLE VI

Differences (°C) Between Transition Temperatures for



with Y=OCOR′ and CO_2R'

X	R'	$T(CO_2R'\text{-}OCOR')^a$	
		melting	clearing
C_1O	C_1	-8.5	---
C_1O	C_3	-34.5	---
C_1O	C_4	-42.5	---
C_2O	C_2	-35.5	---
C_5O	C_1	+5	---
C_5O	C_3	-24	-36
C_5O	C_4	-6	-52
C_6O	C_4	-4.2	-25.8
C_7O	C_1	-61.8	-51.7
C_{10}	C_9	-7.1	---
C_6O	C_9	-13.2	-31.7
$C_{10}O$	C_7	-8.9	-19.7
$C_{10}O$	C_9	0	-22.1
$C_{12}O$	C_9	+3.3	-21.8

a. Data for $R' < C_7$ are from references 17 and 18, data for $Y = OCOR'$, $R' > C_6$ are from reference 2.

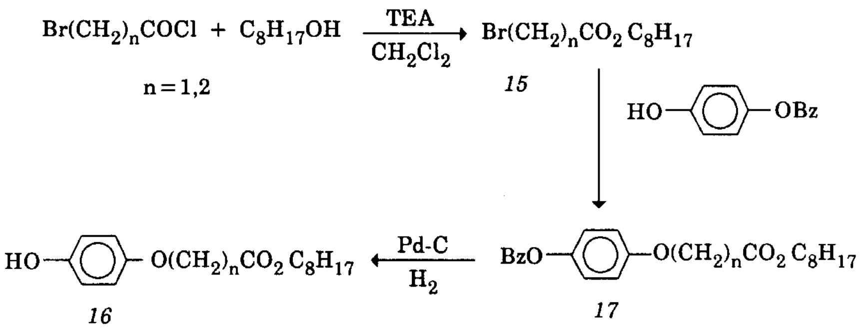
19a n = 1
19b n = 2

when $n = 2$ (Table III). A comparison of melting temperatures of these esters with those not containing the intervening oxygen atom with $Y=(CH_2)_nCO_2R'$ (Table VIII) indicates that the melting temperatures are always higher with the added oxygen atom as would be expected.

TABLE VII

Comparison of Transition Temperatures (°C) for

Y	B	C	A	N	I
$OCOC_7$	132.5	---	153.8	185.5	205.5
OCOC9	126.6	---	149.3	192.2	201.4
CO_2C_7	---	---	69.1	---	144.2
CO_2C_9	---	---	80.7	---	138.3
COC_7	---	108.7	---	178.8	192.9
COC_9	---	104.5	---	---	189.2



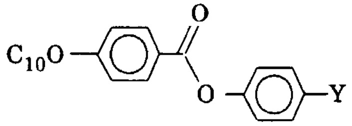
SCHEME 2

DISCUSSION

Thermotropic mesophases occur when it is possible to break the intermolecular forces holding the molecules together in the crystalline lattice in a step-wise manner by applying heat. This requires that these forces vary in strength. In many thermotropic liquid crystals, this is achieved by combining two different structural segments; the rigid core part which usually contains an aromatic ring system and provides strong intermolecular forces and the flexible part which usually consists of aliphatic chains and contributes weaker intermolecular forces. Combinations of ring-ring, chain-chain and ring-chain interactions can then give intermolecular forces of varying intensities. Consideration of these types of interactions has been used to explain how different types of crystalline packing affect the types of mesophases observed in a homologous series of 4-nitrophenyl-4'-*n*-alkoxybenzoates.[19]

TABLE VIII

A Comparison of Melting Temperatures for



Y	mp (°C)
$CH_2CO_2C_9$	52.4
$OCH_2CO_2C_8$	68.2
OC_{10}	70.8
$(CH_2)_2CO_2C_9$	42.6
$O(CH_2)_2CO_2C_8$	70.8
OC_{12}	77.5

$CH_2CO_2C_9$	89.3
$OCH_2CO_2C_8$	99.8
OC_{10}	87
$(CH_2)_2CO_2C_9$	59.1
OC_{12}	90

The problem in studying such relationships is that little is known about how and to what extent various structural features contribute to these forces when they are combined in complex molecules. In the early studies of such relationships, emphasis was placed primarily on the effect of the anisotropy of polarizability which is affected by polar groups and electron conjugation. More recently, it has become obvious that this approach often does not accurately predict mesomorphic properties.[20-22] Our own work on the esters and thioesters supports this conclusion.[1,2,14,23] Since the intermolecular forces are inversely proportional to the distance between molecules, it is not surprising that factors which affect this distance, such as size, shape and chain conformation, must also be considered. Recent research indicates that a better correlation between transition temperatures and molar refractivity which contains a steric factor occurs in some mesogens.[24]

Our modification of the phenylbenzoates to include an ester group in only the phenolic terminal chain *2–4* was initially designed to study the effect of a polar group in this chain on mesomorphic properties. Data for the esters *1–7* indicate that factors other than dipole moment and its effect on the polarization of the molecule must be considered to explain the observed mesomorphic properties. An examination of molecular models (Ealing CPK) of these structures also indicated that the lack of copolarity between the chain and the ring due to steric hindrance between the chain and the ring ortho protons does not explain the observed mesomorphic properties. For example, both coplanarity and dipole moment considerations would predict that the esters with $Y{=}CO_2R'$ would have higher melting temperatures than when $Y{=}OCOR'$. However, this usually is not the case (Table VI). The more sterically hindered esters also tend to show more mesophases suggesting that a larger variation in the strength of the intermolecular forces occurs. In some compounds mesophases were not observed when they were expected. Esters of the type *14* with an additional dipole and higher melting temperatures seem to have strong intermolecular forces but which are all about the same strength so that step-wise melting cannot occur whereas the esters with $Y{=}CH_2CO_2R'$ with low melting temperatures seem to have weak forces of similar intensities which again prevent step-wise melting.

The replacement of tetrahedral carbon atoms with planar divalent oxygen atoms or trivalent carbon atoms introduces another factor for consideration. This kind of substitution increases the flexibility of the chain even when $n = 0$ by removing various restrictions to rotations around single bonds. This is quite evident in the lowered transition temperatures when the ester group is moved away from the ring and no longer constrained by conjugation or steric hindrance with the ring ortho protons. Such increased flexibility allows for more variation in the intermolecular forces as long as these are not weakened too much. The ester chain must then be considered different from the alkyl chain on the acid side so that the intermolecular forces to consider are core-core, core-chain 1, core-chain 2 and chain 1-chain 2. It is obvious that this will also allow for greater variations in packing as well as in intermolecular forces, but this can make it more difficult to find an efficient packing for the molecules. The low crystallization temperatures for the esters *3* and *4* suggest poorer packing efficiencies whereas the small amount of supercooling observed for the esters *14* suggest good packing efficiencies.

This increased flexibility raises the question as to the conformation of the chains in the mesophases. X-ray crystallographic studies of liquid crystals usually show all trans conformations for the terminal chains in the crystalline phase, including those with terminal OCOR′ and CO_2R' groups[25–28] although the R′ chains were usually short. This is not surprising since the all trans conformation is usually the lowest energy state. The occurrence of a regular odd-even alternation in the clearing temperatures of most homologous series of liquid crystals, including the phenylbenzoates,[7] suggest the predominance of the all trans conformation in the mesophases as well.[29] Other studies not only indicate the presence of gauche conformers but that these increase as the temperature increases and therefore they also increase in the mesophases.[30–32] We know that the series with $Y{=}OCOR'$ shows a regular odd-even alternation of the clearing temperatures,[2] but not enough data are available to determine this for the series with $Y{=}(CH_2)_nCO_2R'$. Whether or not the gauche conformers predominate in the liquid crystal phase, they could still be present in larger amounts when $n = 2$ than when $n = 0$. It would be interesting to determine if the odd-even alternation of the clearing temperatures occurred in the $Y{=}(CH_2)_nCO_2R'$ series. Recently, x-ray studies of some biphenyl-phenyl esters containing an alkoxy and a branched alkyl chain as the two terminal chains show an all trans C_6O chain in the crystalline phase but a gauche conformation at the α—β C—C bond for the C_7O chain.[33] Also, the bulky branched chain is highly disordered for the C_5O ester but only slightly disordered in the C_7 homolog. Thus, the length of the terminal chains also seems to affect the conformation of a particular chain or even the other chain in the crystalline phase.

EXPERIMENTAL

Anhydrous Na_2SO_4 was used to dry all organic extracts. The Pd/C catalysts were obtained from Strem Chemical Co. 4-Benzyloxybenzoic acid was prepared by alkylation of 4-hydroxybenzoic acid methyl ester using our DMF/benzene procedure followed by basic hydrolysis.[9] Purified yields were 87.0% (ester, from abs EtOH) and 79.3% (acid, from Me_2CO). Our mps of 98–100° (ester) and 192–197° (acid) agreed with those reported.[34,35] NMR data are as follows: ester ($CDCl_3$) δ8.10 (d, $J = 9.0$ Hz, 2, ArH ortho to CO_2Me), 7.49 (s, 5, C_6H_5), 7.08 (d, $J = 9.0$ Hz, 2, ArH ortho to RO), 5.14 (s, 2, CH_2) and 3.90 (s, 3, CH_3) and acid (DMSO-d_6) δ7.97 (d, $J = 9.0$ Hz, 2, ArH ortho to acid), 7.50 (s, 5, C_6H_5), 7.14 (d, $J = 9.0$ Hz, 2, ArH ortho to OR) and 5.20 (s, 2, CH_2).

TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with $CHCl_3$ as the solvent and UV light and I_2 as the detectors. All compounds were purified until they showed only one spot by TLC. Flash chromatography was done on Aldrich grade 60 (mesh 230–400) silica gel. Melting points (°C) were determined using a Thomas-Hoover melting point apparatus and are corrected. The elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

IR spectra were run on a Pye-Unicam 3-200 instrument. NMR spectra were obtained using a Varian EM-360, General Electric GN300 instrument (GN) or Varian RT80 (FT) instrument with TMS as the internal standard. Proton assignments were made primarily on the basis of our experience with spectra for many substituted phenylbenzoates and their precursors and the spectra for phenylpropionic acid reported in References 36 and 37.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/min as described previously.[38] Samples were cooled at 2°/min until they crystallized to obtain the crystallization temperature and so no monotropic phases occurring before this temperature were missed. Temperatures for monotropic phases (indicated by parentheses in the Tables) were obtained by reheating these phases. Abbreviations used for phases are K=crystal, N=nematic, I=isotropic liquid and B, C, and A indicate smectic phases with these identifications. Mesophases were identified by the typical textures observed for these phases.[39,40] No determination of the type of B phase observed could be made by microscopy since these did not occur below a smectic phase. DSC scans were run on a Perkin-Elmer DSC-2 at 2.5°/min.

3-(p-Hydroxyphenyl)propionic Acid 8 (n = 2, X=H). A stirred mixture of 4-hydroxycinnamic acid (100 g, 0.61 mole) and 10 g of 5% Pd/C in tetralin (500 ml) was refluxed for 2 hr.[41] Ether (600 ml) was added to the cooled (RT) reaction mixture and the catalyst removed by filtration through Celite. The filtrate was extracted with 10% aq NaOH soln (3 × 200 ml) and the basic layer washed with Et_2O (500 ml), made acidic with concd HCl and cooled in an ice bath. The resulting precipitate was collected by filtration, washed with H_2O and dried to give 84.9 g (83.9%) of the crude product. Recrystallization of this material twice from 3<u>N</u>HCl gave 72.0 g (71.1%) of the purified acid *8*: mp 122–125°, (lit mp 120–121° [41]) TLC R_f = 0.01 and IR (Nujol) 3300 (wk OH), 1680 (str CO_2H) and 1590 cm^{-1} (str Ar).

4-Benzyloxyphenylacetic Acid 9 (n = 1). The acid *8* (*n* = 1) (50.0 g, 0.33 mole) was added in small portions to a stirred soln of KOH (40.5 g, 0.72 mole) in H_2O (82 ml) and EtOH (650 ml) at RT followed by benzylbromide (56.3 g, 0.33 mole) (dropwise). The rxn mixture was refluxed for 20 hr, 10% aq KOH (100 ml) added and refluxing continued for an additional 2 hr. The EtOH was removed by distillation and the residue dissolved in H_2O (650 ml). This soln was washed with Et_2O, acidified with 36% HCl and the resulting precipitate collected by filtration, washed with H_2O and dried at 70°. The crude acid was recrystallized from abs EtOH to give 54.0 g (67.8%) of the purified acid *9* (*n* = 1): TLC ($CHCl_3$) R_f = 0.06 (R_f for starting phenol = 0) mp 124° (lit mp 120–121° [42]) and IR (Nujol) 3100–2800 (br acid OH), 1705 (str CO_2H) and 1608 cm^{-1} (Ar) and NMR (DMSO-d_6) δ7.21 (s, 5, C_6H_5), 7.02 (d, 2, *J* = 8.0 Hz, ArH ortho to CH_2), 6.77 (d, 2, *J* = 8.0 Hz, ArH ortho to OR), 4.89 (s, 2, OCH_2) and 3.31 (s, 2, CH_2). The acid with *n* = 2 was prepared in the same manner: mp 115–120.5° (lit mp 123–124° [43]), NMR (GN) (acetone-d_6) δ7.51–7.28 (m, 5, C_6H_5), 7.18 (d, 2, *J* = 7.5 Hz, ArH ortho to CH_2), 6.93 (d, 2, *J* = 7.0 Hz, ArH ortho to RO), 5.07 (s, 2, OCH_2), 2.85 (t, *J* = 7.5, 2, $ArCH_2$), and 2.57 (t, *J* = 7.1, 2, CH_2CO_2).

Nonyl-4-benzyloxyphenylacetate 11 (n = 1, R'=C_9H_{19}). To a stirred soln of the acid *9* (*n* = 1) (2.42 g, 10.0 mmoles), nonanol (1.44 g, 10.0 mmoles) and *p*-TSA (82 mg) in 8 ml pyridine was added all at once DCC (2.07 g, 10.0 mmole). This mixture was refluxed 2 hr, cooled to RT and filtered to remove DCU. The filtrate was washed with H_2O, 5% aq KOH and H_2O; dried, filtered and the filtrate rotovaped. Recrystallization of the residue twice from abs EtOH gave 1.53 g (46.6%) of the purified ester *11* (*n* = 1, R'=C_9H_{19}): mp. 36.0–37.5°, IR ($CHCl_3$) no OH, 1725 (str, CO_2R) and 1620, 1590 cm^{-1} (wk, Ar) and NMR (CCl_4) δ7.20 (s, 5, C_6H_5), 7.05 (d, *J* = 9.0 Hz, 2, ArH ortho to CH_2CO_2), 6.72 (d, *J* = 8.5, 2, ArH ortho to O), 4.88 (s, 2, $PhCH_2$), 3.92 (t, *J* = 6.0 Hz, 2, CO_2CH_2), 3.34 (s, 2, $ArCH_2CO_2$), and 1.61–0.67 (m, 17, C_8H_{17}).

The ester with <u>*n* = 0</u>, <u>R'=C_9H_{19}</u>: m.p. 42.0–44.0°, and NMR (CCl_4) δ7.94 (d, *J* = 9.0 Hz, 2, <u>ArH ortho to CO_2R</u>) 7.36 (s, 5, C_6H_5), 6.95 (d, *J* = 9.0 Hz, 2, ArH ortho to RO), 5.09 (s, 2, $PhCH_2$), 4.24 (t, J = 6.0 Hz, 2, CO_2CH_2) and 2.09–0.63 (m, 17, C_8H_{17}), and the ester with $n = 1$, $R'{=}C_7H_{15}$: bp 210° (1.5 mm) and NMR (CCl_4) δ7.25 (s, 5, C_6H_5), 7.10 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 6.78 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.93 (s, 2, $PhCH_2$), 3.98 (t, J = 7.0 Hz, 2, CO_2CH_2), 3.40 (s, 2, $ArCH_2CO_2$) and 1.80–0.62 (m, 13, C_6H_{13}) was prepared in the same manner but the ester with $n = 2$, $R'{=}C_7H_{15}$: NMR ($CDCl_3$, GN) 7.46–7.26 (m, 5, C_6H_5), 7.11 (d, J = 8.6 Hz, 2, ArH ortho to CH_2), 6.89 (d, J = 8.9 Hz, 2, ArH ortho to OR), 5.02 (s, 2, $PhCH_2$), 4.05 (t, J = 7.0 Hz, 2, CO_2CH_2), 2.89 (t, J = 7.7 Hz, 2, $ArCH_2$), 2.58 (t, J = 7.7 Hz, 2, CH_2CO_2), 1.67–1.53 (m, 2, OCH_2CH_2), 1.28 (br s, 8, $4CH_2$) and 0.88 (t, J = 6.0 Hz, 3, CH_3) was prepared using the standard carbodiimide procedure[2] but with more CH_2Cl_2, refluxing for 3 hr and stirring at RT for 17 hr. The crude product (quant yield) was purified by flash chromatography using CH_2Cl_2 to give a pale yellow liquid (yield 92.5%).

4-Methoxycarbonyl Acids 10. These were prepared using the procedure of Chin and Goodby[10] without modification in purified yields of 70–88%: $n = 0$, mp 177–178°* (abs EtOH) and NMR (acetone-d_6) δ8.10 (d, J = 9.0 Hz, 2, ArH ortho to CO_2H), 7.48 (s, 1, CO_2H), 7.25 (d, J = 9.0 Hz, 2, ArH ortho to O) and 3.85 (s, 3, Me); $n = 1$, mp 94–96° (H_2O), IR ($CHCl_3$) 3500–2400 (br acid OH), 1740 (str CO_2R), 1690 (str CO_2H) and 1600 cm^{-1} (wk Ar) and NMR ($CDCl_3$) δ7.38 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 7.20 (d, J = 9.0 Hz, 2, ArH ortho to O), 3.89 (s, 3, OMe) and 3.64 (s, 2, CH_2); and $n = 2$, mp 81–83° (3NHCl), IR same as n = 1 and NMR (CCl_4) 7.10 (s, 4, ArH), 3.80 (s, 3, MeO), 2.78 (t, J = 6.0 Hz, 2, $ArCH_2$) and 2.68 (t, J = 6.0 Hz, 2, CH_2CO_2).

4-Methoxycarbonyloxy Esters 12. These were prepared by converting the acids to the acid chlorides with $SOCl_2$ followed by esterification in Et_3N/CH_2Cl_2. All these esters were liquids at RT and were purified by flash chromatography using 3% EtOAc in hexane as the eluting solvent. Purified yields ranged from 75.0–91.9% and IR (film) 1780 ($MeOCO_2$) and 1735 cm^{-1} (CO_2R) for all these esters and NMR ($CDCl_3$) for $n = 0$, $R'{=}C_9H_{19}$: δ8.20 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.34 (d, J = 9.0 Hz, 2, ArH ortho to O), 4.35 (t, J = 6.0 Hz, 2, CO_2CH_2), 3.93 (s, 3, Me) and 2.10–0.6 (m, 17, C_8H_{17}).

Nonyl-4-hydroxybenzoate 13 ($n = 0$, $R'{=}C_9H_{19}$). A soln of the benzyl ether 9 (n = 0, 16.1 g, 45.5 mmoles) in abs EtOH (250 ml) containing 5% Pd-C (4.0 g) was hydrogenated for 2 hr at 40° and 50 psi. The catalyst was removed by filtration through Celite on glass fiber filter paper and the solvent removed from the filtrate *in vacuo* to give 9.9 g (82.5%) of the phenol *13* (n = 0, $R'{=}C_9H_{19}$) bp 190–210° (0.4 mm), the phenol with n = 0, $R'{=}C_7H_{15}$ was also prepared in this manner but was purified in a yield of 98.8% by chromatography on silica gel using CH_2Cl_2 as the eluting solvent.

A soln of the methoxycarbonyl ester *12* (n = 0, $R'{=}C_9H_{19}$ (67.3 g, 0.23 mole)

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* Chin and Goodby reported a mp of 84.8°, but we feel this is an unlikely value and probably an error.

in a mixture of abs EtOH (200 ml) and concd NH_4OH (100 ml) was stirred at RT for 1 hr, acidified with concd HCl and extracted with Et_2O. The organic layer was washed with H_2O (2 ×), satd $NaHCO_3$ soln (3 ×) and H_2O (3 ×); dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave 51.2 g (85.4%) of the crude product. This material was flash chromatographed using 20% EtOAc in hexane as the eluting solvent and then recrystallized from hexane to give 49.5 g (82.6%) of the purified phenol *13* ($n = 0$, $R'{=}C_9H_{19}$): mp 43.5–44.0°, IR 3380 (str, br OH), 1690 (str CO_2R) and 1620, 1595 cm^{-1} (med Ar) and NMR ($CDCl_3$, GN) δ7.87 (d, J = 10.3 Hz, 2, ArH ortho to CO_2R), 6.83 (d, J = 7.4 Hz, 2, ArH ortho to OH), 4.99 (br s, 1, OH), 4.23 (t, J = 6.7 Hz, 2, CO_2CH_2), 1.72 (t, J = 6.4 Hz, 2, OCH_2CH_2), 1.49–1.15 (m, 12, $6CH_2$) and 0.95–0.85 (m, 3, CH_3). *Anal Calcd* for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.72; H, 9.03.

Cleavage of other methoxycarbonyloxy esters *12* was done using this procedure. The phenol *13* with $n = 0$, $R'{=}C_7H_{15}$ had mp = 47.0–48.5°. When n = 1 or 2, the phenols were liquids. Distillation gave the following boiling points: $n = 1$ ($R'{=}C_9$) 184° (0.6 mm) and $n = 2$ ($R'{=}C_7$) 160° (0.4 mm). The others were purified by flash chromatography using 20% EtOAc in hexane as the eluting solvent. NMR for $n = 1$ ($R'{=}C_9$) in CCl_4: δ7.11 (distorted d, J = 8.0 Hz, 3, OH and ArH ortho to CH_2), 6.72 (d, J = 8.0 Hz, 2, ArH ortho to OH), 4.11 (t, J = 6.0 Hz, 2, CO_2CH_2), 3.55 (s, 2, $ArCH_2$) and 2.52–0.78 (m, 17, C_8H_{17}) and $n = 2$ ($R'{=}C_8$) in $CDCl_3$ (FT): δ7.03 (d, J = 7.82 Hz, 2, ArH ortho to CH_2), 6.35 (d, J = 7.46 Hz, 2, ArH ortho to OH), 5.28 (s, 1, OH), 4.07 (t, J = 6.39 Hz, 2, CO_2CH_2) 2.87 (t, J = 7.61 Hz, 2, $ArCH_2$), 2.60 (t, J = 7.58 Hz, 2, CH_2CO_2), 1.60 (t, 6.36, 2, OCH_2CH_2), 1.28 (s, 10, $5CH_2$) and 0.86–0.91 (m, 3, CH_3).

Octyl(4'-benzyloxyphenoxy)acetate 17 (n = 1). A stirred mixture of 4-benzyloxyphenol (10.0 g, 0.05 mole), NaOH (2.0 g, 0.05 mole) and molecular sieves (10 g, Linde #4A) in 1:1 DMF:benzene (45 ml) was refluxed using a Dean-Stark trap until the distillate was no longer cloudy. Octylbromoacetate (*15*) (12.6 g, 0.05 mole), prepared by esterification of bromoacetyl chloride with octanol in CH_2Cl_2 was added dropwise and refluxing continued for an additional 6 hr. The insoluble solid was removed by filtration and washed with $CHCl_3$. The solvent was removed from the filtrate *in vacuo* and the residue dissolved in $CHCl_3$, washed with 10% aq KOH and H_2O, dried and filtered. Removal of the solvent from the filtrate followed by recrystallization from abs EtOH gave 12.0 g (64.9%) of the purified ether *17*: mp 47.5–51.0°, TLC ($CHCl_3$) showed one spot with R_f = 0.62; IR (Nujol) 1740 (str CO_2R) and 1600 cm^{-1} (weak Ar) and NMR ($CDCl_3$) δ7.35 (s, 5, C_6H_5), 6.88 (s, 4, ArH), 4.98 (s, 2, $PhCH_2$), 4.52 (s, 2, OCH_2CO_2), 4.17 (t, J = 6.0 Hz, 2, CO_2CH_2) and 1.99–0.60 (m, 15, C_7H_{15}).

Octyl(4'-hydroxyphenoxy)acetate 16 (n = 1). This compound was prepared using the catalytic reduction method as described for nonyl-4-hydroxybenzoate. Recrystallization of the crude product from ligroine (60–80°) gave 3.18 g (84.7%) of the purified phenol *16* (n = 1): mp 42.0–44.5°; IR (Nujol) 3460 (str OH), 1735 (str CO_2R) and 1605 cm^{-1} (med Ar) and NMR ($CDCl_3$): δ6.78 (s, 4, ArH), 4.52 (s, 2, OCH_2CO_2), 4.12 (t, J = 6.0 Hz, 2, CO_2CH_2) and 2.02–0.43 (m, 15, C_7H_{15}). *Anal. calcd* for $C_{16}H_{24}O_4$: C, 68.54, H, 8.60: Found: C, 68.44 and H, 8.35.

Octyl-2-bromopropionate 15 (n = 2). Refluxing 3-bromopropionic acid (30.6 g, 0.20 mole) with 16 ml $SOCl_2$ for 1 hr gave the acid chloride (24.2 g, 71.0%) with b.p. 83–84° (20 mm). A soln of this liquid (0.14 mole) in dry CH_2Cl_2 (100 ml) was added dropwise to a stirred ice cooled soln of octanol (18.2 g, 0.14 mole) and Et_3N (20.2 g, 0.20 mole) in dry CH_2Cl_2 (250 ml). This mixture was allowed to warm to RT and stirring continued for 1 hr. It was then washed with 5% aq $NaHCO_3$ soln and H_2O, dried and filtered. Removal of the solvent from the filtrate *in vacuo* gave 48.3 g (95.8%) of the crude product. Distillation of this liquid at 115–120° (10 mm) gave 30.8 g (83.0%) of the purified ester *15* (*n* = 2): IR (film), 1720 cm^{-1} (str, CO_2R).

Octyl-2-(4'-benzyloxyphenoxy)propionate 17 (n = 2). A mixture of 4-benzyloxyphenol (10.0 g, 50 mmoles), the bromo ester *15* (*n* = 2, 15.9 g, 60 mmoles) and anhyd K_2CO_3 (14.0 g, 100 mmole) in dry acetone (200 ml) was refluxed for 48 hr. More of the bromo ester (10.6 g, 40 mmoles) was added and refluxing continued for 30 hr. This mixture was then cooled to RT and filtered. The solvent and excess bromo ester were removed by vacuum distillation. Filtration of the residue through a short column of silica gel (50 g) using 5% EtOAc in hexane as the eluting solvent gave 4.6 g (24.0%) of the crude product. Recrystallization of this material from abs EtOH gave 3.9 g (20.3%) of the purified ether: mp 52.0–55.0°; TLC (8% EtOAc in hexane) showed a single spot with R_f = 0.26 (4-benzyloxyphenol R_f = 0.05 and the bromoester R_f = 0.46); IR ($CHCl_3$) 1720 (str, CO_2R) and 1580 cm^{-1} (wk Ar) and NMR (CCl_4) δ7.25 (s, 5, C_6H_5), 6.70 (s, 4, ArH), 4.90 (s, 2, $Ph\underline{CH_2}$), 4.05 (t, *J* = 6.0 Hz, 2, CO_2CH_2), 4.00 (t, *J* = 6.0 Hz, 2, $ArO\underline{CH_2}$), 2.61 (t, *J* = 6.0 Hz, 2, CH_2CO_2) and 1.92–0.70 (m, 15, C_7H_{15}).

Octyl-3(4'-hydroxyphenoxy)propionate 16 (n = 2). This compound was prepared using the catalytic reduction procedure described for preparing nonyl-4-hydroxybenzoate except 10% Pd-C was used for 3 hr. Recrystallization of the crude product (2.7 g, 91.8%) from Et_2O-hexane gave 2.4 g (81.6%) of the purified phenol: mp 52.0–54.5° TLC (4% abs EtOH in $CHCl_3$) showed a single spot with R_f = 0.40 (starting ether R_f = 0.75); IR (Nujol) 3350 (str OH), 1730 (str CO_2R) and 1610 cm^{-1} (wk Ar) and NMR (CCl_4) δ6.55 (s, 4, ArH), 4.03 (t, *J* = 6.0 Hz, 4, $2OCH_2$), 2.65 (t, *J* = 6.0 Hz, 2, CH_2CO_2) and 1.90–0.65 (m, 15, C_7H_{15}).

The *phenylbenzoates 2–4* and *cyclohexane diesters 5–7* were prepared by esterification of the phenols with the appropriate acids using the carbodiimide or acid chloride methods as previously described.[2] Initial purification was by recrystallization from abs EtOH except for *2* ($X{=}C_6O$, $R'{=}C_7$) which was recrystallized from ligroine (60–90°). However, several of these esters contained trace impurities which gave wide clearing temperatures. These were purified by flash chromatography using EtOAc-hexane as the eluting solvent for the phenylbenzoates and CH_2Cl_2 for the cyclohexane diesters until the clearing temperatures were sharp. IR spectra for the phenylbenzoates showed a single strong ester absorption at 1700–1710 cm^{-1} and an aromatic peak at 1610 cm^{-1} (med str) whereas spectra for the cyclohexane diesters showed 2 intense ester peaks at 1760 and 1710 and a strong aromatic peak at 1600 cm^{-1}. Typical NMR data for the phenylbenzoates are as follows: *2* ($X{=}C_{10}H_{21}O$, $R'{=}C_9H_{19}$) ($CDCl_3$, GN) δ8.18–8.08 (m, 4, ArH ortho to CO_2R), 7.28 (d, J = 8.3 Hz, 2, ArH ortho to O), 6.96 (d, J = 9.2 Hz, 2, ArH ortho to OC_{10}), 4.32 (t, J = 6.4 Hz, 2, CO_2CH_2), 4.02 (t, J = 6.4 Hz, 2, OCH_2), 1.88–1.70 (m, 4, $OCH_2\underline{CH_2}$), 1.53–1.19 (m, 26, CH_2) and 0.88 (t, J = 6.1 Hz, 6, CH_3); *3* ($X{=}C_{10}H_{21}$, $R'{=}C_9H_{19}$) (CCl_4) δ8.14 (d, J = 8.0 Hz, 2, ArH ortho to CO_2R), 7.30 (d, J = 8.0 Hz, 2, ArH ortho to CH_2CO_2), 7.22 (d, J = 8.0 Hz, 2, ArH ortho to CH_2) 7.18 (d, J = 8.0 Hz, 2, ArH ortho to OCO) 4.07 (t, J = 6.0 Hz, 2, OCH_2), 3.58 (s, 2, $Ar\underline{CH_2}CO_2$), 2.72 (t, J = 7.0 Hz, 2, $ArCH_2$) and 2.02–0.70 (m, 36, C_8H_{17} and C_9H_{19}); *3* ($X{=}C_{10}H_{21}O$, $R'{=}C_9H_{19}$) (CCl_4) δ8.18 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R) 7.22 (d, J = 9.0 Hz, 2, ArH ortho to CH_2CO_2), 7.13 (d, J = 9.0 Hz, 2, ArH ortho to O), 6.89 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.03 (m, 4, OCH_2), 3.54 (s, 2, CH_2CO_2) and 2.30–0.60 (m, 36, C_8H_{17} and C_9H_{19}); *4* ($X{=}C_{10}H_{21}O$, $R'{=}C_7H_{15}$) (CCl_4): δ8.10 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.14 (s, 4, ArH ortho to OCO and CH_2) 6.89 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.00 (t, J = 6.0 Hz, 4, OCH_2), 2.81 (t, J = 6.0 Hz, 2, $ArCH_2$), 2.65 (t, J = 6.0 Hz, 2, CH_2CO_2) and 2.0–0.68 (m, 32, C_9H_{19} and C_6H_{13}); *14a* ($R{=}C_{10}H_{21}O$, $R'{=}C_8H_{17}$) (CCl_4) δ8.05 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.06 (d, J = 9.0 Hz, 2, ArH ortho to OCO), 6.84 (d, J = 9.0 Hz, 2, acidic ArH ortho to OR), 6.79 (d, J = 9.0 Hz, 2, phenolic ArH ortho to OR), 4.90 (s, 2, OCH_2CO_2), 4.09 (t, J = 6.0 Hz, 2, CO_2CH_2), 3.99 (t, J = 6.0 Hz, 2, OCH_2) and 2.10–0.5 (m, 34, C_7H_{15} and C_9H_{19}) and *14b* ($R{=}C_{10}H_{21}O$, $R'{=}C_8H_{17}$) (CCl_4) δ8.07 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.05 (d, J = 9.0 Hz, 2, ArH ortho to OCO), 6.84 (d, J = 9.0 Hz, 2, acidic ArH ortho to OR) 6.79 (d, J = 9.0 Hz, 2, phenolic ArH ortho to OR), 4.37–3.80 (m, 6, $3OCH_2$), 2.78 (t, J = 7.0 Hz, 2, CH_2CO_2) and 2.06–0.66 (m, 34, C_7H_{15} and C_9H_{19}). NMR spectra for the cyclohexane diesters are as follows: *5* ($R'{=}C_9H_{19}$) ($CDCl_3$) δ7.25 (d, J = 9.0 Hz, 4, ArH ortho to CO_2R), 6.30 (d, J = 9.0 Hz, 4, ArH ortho to OCO), 3.43 (t, J = 6.0 Hz, 4, OCH_2) and 1.94–0.0 (m, 44, aliphatic); *6* ($R'{=}C_9H_{19}$) ($CDCl_3$, GN) δ7.30 (d, J = 7.61 Hz, 4, ArH ortho to CH_2), 7.03 (d, J = 8.58 Hz, 4, ArH ortho to OCO), 4.07 (t, J = 6.50 Hz, 4, CO_2CH_2), 3.60 (s, 4, $Ar\underline{CH_2}CO_2$), 2.58 (br s, 2, 1,4 cyclohex), 2.28 (d, J = 7.54 Hz, 4, Equation cyclohex), 1.69–1.59 (m, 8, $CO_2CH_2\underline{CH_2}$ and ax. cyclohex), 1.26 (s, 24, CH_2), and 0.88 (m, 6, CH_3); *7* ($R'{=}C_9H_{19}$) ($CDCl_3$, GN) δ7.21 (d, J = 10.56 Hz, 4, ArH ortho to CH_2), 6.99 (d, J = 7.06 Hz, 4, ArH ortho to OCO), 4.06 (t, J = 6.57 Hz, 4, CO_2CH_2) 2.94 (t, J = 7.57 Hz, 4, $ArCH_2$), 2.61 (t, J = 7.70, 6, CH_2CO_2 and 1,4 cyclohex), 2.28 (d, J = 7.57 Hz, 4, Equation cyclohex), 1.69–1.60 (m, 8, $CO_2CH_2\underline{CH_2}$ and ax. cyclohex), 1.27 (s, 24, CH_2) and 0.88 (m, 6, CH_3); *19a* ($R'{=}C_8H_{17}$) ($CDCl_3$, GN) δ6.99 (d, J = 8.73 Hz, 4, ArH ortho to OCO), 6.90 (d, 8.92, 4, ArH ortho to OR), 4.60 (s, 4, OCH_2CO_2), 4.19 (t, J = 6.58 Hz, 4, CO_2CH_2), 2.56 (br s, 2, 1,4 cyclohex), 2.26 (d, J = 7.90 Hz, 4, Equation cyclohex), 1.68–1.58 (m, 8, $CO_2CH_2\underline{CH_2}$ and ax. cyclohex), 1.28 (s, 20, CH_2) and 0.88 (m, 6, CH_3) and *19b* ($R'{=}C_8H_{17}$) ($CDCl_3$, GN) 6.97 (d, J = 8.35 Hz, 4, ArH ortho to OCO), 6.88 (d, J = 8.29 Hz, 4, ArH ortho to OR), 4.22 (t, J = 6.14 Hz, 4, CO_2CH_2), 4.12 (t, J = 6.69 Hz, 4, $ArOCH_2$), 2.77 (t, J = 6.32, 4, CH_2CO_2), 2.56 (br s, 2, 1,4 cyclohex), 2.26 (d, J = 8.28 Hz, 4, Equation cyclohex), 1.68–1.59 (m, 8, $CO_2CH_2\underline{CH_2}$, and ax. cyclohex), 1.30–1.27 (m, 20, CH_2), and 0.90–0.86 (m, 6, CH_3).

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