Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates. 5. Phenylbenzoates Containing a $(CH_2)_n0_2CR'$ Group (n=1,2) on the Phenolic End

M. E. Neubert [a], C. M. Citano [a], M. C. Ezenyilimba [a b c], M. R. Jirousek [a b c], S. Sabol-keast [a] & R. B. Sharma [a b c]

[a] Liquid Crystal Instituted and Chemistry Departments, Kent State University, Kent, OH, 44242

[b] Chemistry Department, Eastman Kodak Chemical Co., Harvard University, K. L., Uniroyal, Mishawaka, IN; MRJ, Cambridge, MA; MCE, Rochester, NY

[c] RBS, Day Chemical Laboratories, Inc., Fairborn, OH

Version of record first published: 24 Sep 2006.

To cite this article: M. E. Neubert , C. M. Citano , M. C. Ezenyilimba , M. R. Jirousek , S. Sabol-keast & R. B. Sharma (1991): The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates. 5. Phenylbenzoates Containing a $(CH_2)_n0_2CR'$ Group (n=1,2) on the Phenolic End, Molecular Crystals and Liquid Crystals, 206:1, 103-116

To link to this article: http://dx.doi.org/10.1080/00268949108037722

Mol. Cryst. Liq. Cryst., 1991, Vol. 206, pp. 103–116
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Printed in the United States of America

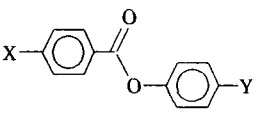
The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Phenylthiobenzoates. 5. Phenylbenzoates Containing a $(CH_2)_nO_2CR'$ Group (n = 1,2) on the Phenolic End

M. E. NEUBERT,†‡ C. M. CITANO,†‡ M. C. EZENYILIMBA,†‡* M. R. JIROUSEK,†‡* S. SABOL-KEAST and R. B. SHARMA†*

Liquid Crystal Institute† and Chemistry Department,‡ Kent State University, Kent, OH 44242

(Received December 26, 1989; in final form March 18, 1991)

A few homologs of the esters *2* (R′ = C_8H_{17}, n = 1 or 2) and *4* (R′ = C_7H_{15})



1	$Y=(CH_2)_nCO_2R'$,	n = 0-2
2	$Y=(CH_2)_nOCOR'$,	n = 0-2
3	$Y=O(CH_2)_nCO_2R'$,	n = 1,2
4	$Y=O(CH_2)_nOCOR'$,	n = 2

were synthesized and their mesomorphic properties determined using hot-stage polarizing microscopy. No mesophases were observed for series *2* (n = 1) or *4*. This was also true for the previously reported series *1* (n = 1) and *3*. Transition temperatures for series *2* with n = 2 were lower than when n = 1 but higher than for the reverse ester series *1* with n = 2. In both series *1* and *2* with n = 2, only short range monotropic phases were observed. Like its parent series *2* (n = 0), the n = 2 esters showed various combinations of nematic and smectics A, B and C, whereas the reverse esters *1* (n = 2) have only nematic and smectic A phases.

The phenols required for synthesizing the esters *2* (n = 2) and *4* were prepared from the analogous protected phenolic alcohols. No suitable protecting group which could be selectively removed from the

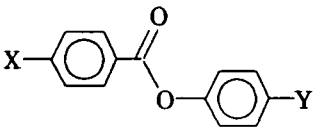
* Current addresses: K.L., Uniroyal, Mishawaka, IN; MRJ, Chemistry Department, Harvard University, Cambridge, MA; MCE, Eastman Kodak Chemical Co., Rochester, NY; and RBS, Day Chemical Laboratories, Inc., Fairborn, OH.

phenol could be found for synthesizing the precursor alcohol for series *2* when n = 1. Instead these esters were prepared by esterification of the appropriately 4-substituted benzoic acid with 4-hydroxybenzaldehyde, reduction to the alcohol and esterification. NMR spectra were used to confirm the structures of all intermediates and esters.

Keywords: liquid crystals, phenylbenzoates, 4-substituted phenols, NMR

INTRODUCTION

Earlier, we reported the effect of adding spacer methylene groups to a carboxylate group in the phenylbenzoates *1* (n = 1 or 2)



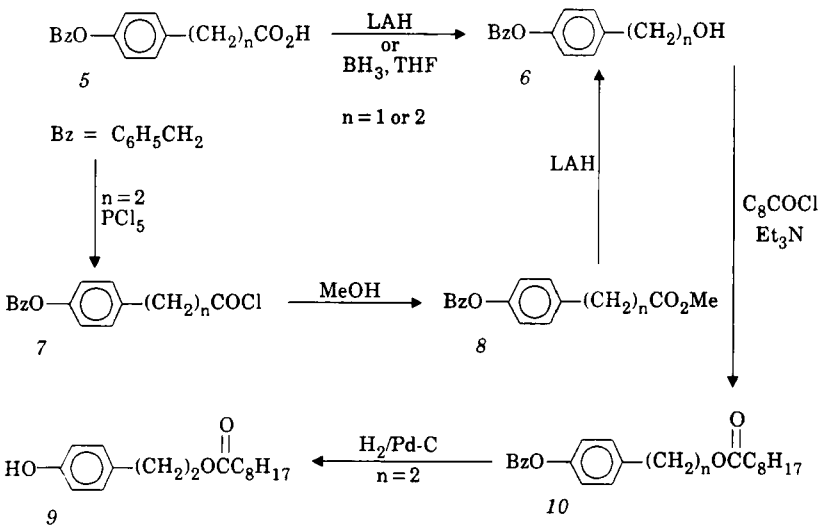
1	$Y=(CH_2)_nCO_2R'$,	n = 0-2
2	$Y=(CH_2)_nOCOR'$,	n = 0-2
3	$Y=O(CH_2)_nCO_2R'$,	n = 1,2
4	$Y=O(CH_2)_nOCOR'$,	n = 2

on mesomorphic properties as compared to when the carboxylate group is attached directly to the ring *1* (n = 0).[1] We were interested in determining if reversing the ester group in the chain containing spacer groups (n = 1 or 2) would increase the number of mesophases observed in the esters *2* (n = 1, 2) as occurs when no spacer group is present *2* (n = 0).[2] Thus, a few homologs of this series with n = 1 and 2 were prepared for comparison of their mesomorphic properties with those for series *2* (n = 0) and *1*. In our earlier work, we prepared the esters *3* which contained an intervening oxygen atom so we also synthesized one of the esters in series *4* for comparison.

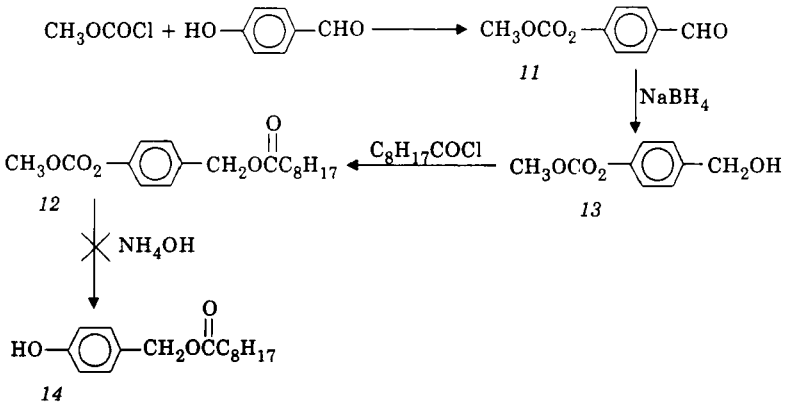
SYNTHESIS

The phenol *9* was prepared using the methods shown in Scheme I. The benzyloxy propionic acid *5* (n = 2) was reduced using either LAH or BH_3 to give the alcohol *6* directly or by LAH reduction of the methyl ester *8*. Esterification with nonanoyl chloride gave the benzyloxy protected ester *10* which was hydrogenated to the phenol *9*. This method could also be used to prepare the ester with n = 1 but hydrogenolysis occurred at both benzyl-oxygen bonds to give 4-hydroxybenzene ethanol. An attempt to prepare the n = 1 alcohol using the methoxycarbonate protecting group also did not give selective cleavage of the protecting group (Scheme II). The n = 1 ester chain was incorporated into the phenylbenzoates by the method shown in Scheme III which, although successful, does not provide a single intermediate that can be used to prepare esters with a variety of X substituents. The phenol *22* needed to prepare the esters *4* was also prepared by alkylating 4-benzyloxyphenol with the bromide *21* (Scheme IV).

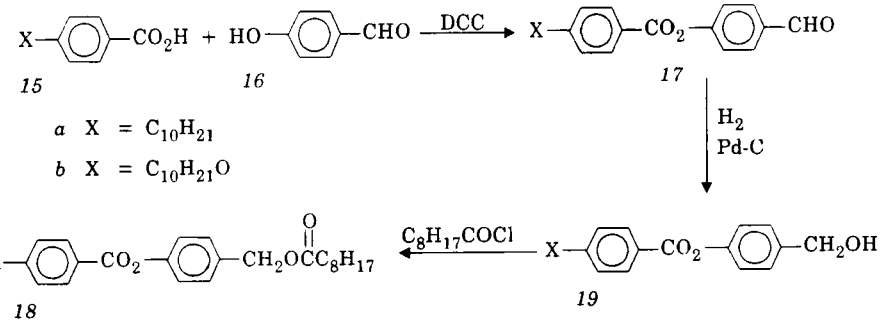
The esters *2* and *4* (n = 2) were prepared by esterification of the appropriate



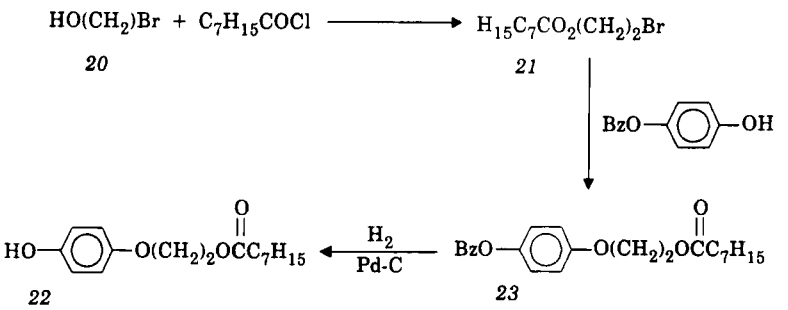
SCHEME I



SCHEME II



SCHEME III



SCHEME IV

acid with the phenols using the carbodiimide method as previously reported.[2] The purity of all compounds was checked by TLC and if necessary by HPLC. All materials were purified until they showed only one spot by TLC. The purity of the phenylbenzoates was also monitored by the range of their clearing temperatures which were <1°. Structures were confirmed by NMR. Typical examples of NMR data are given in the experimental section. Data for the alkyl/alkoxyphenylbenzoates reported earlier[3] were used to aid in identifying peaks in these new esters along with Aldrich reference curves for 4-methylbenzyl alcohol,[4a] p-benzyloxybenzyl alcohol[4b] and benzyl acetate.[4c] Typical examples of the procedures used are also given in the experimental section.

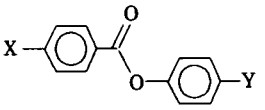
MESOMORPHIC PROPERTIES

Mesomorphic properties, as determined by hot-stage polarizing microscopy, are presented in Table I. Abbreviations used for phases are defined in the experimental section. No mesophases were observed in either the esters *2* (n = 1) or *4*. The same trend was observed in the reverse ester series *1* and *3*. When n = 2, mesophases were observed, but all of these were monotropic as was also true in the reverse ester series. A comparison of the mesomorphic properties of the esters *2* (n = 2) with those for the esters without a spacer group *2* (n = 0) and the reverse esters *1* (n = 2) is made in Figure 1. An attempt has been made to use a Y chain containing the same number of atoms for comparison, although it is not certain this makes the best comparison. The limited amount of data restricts the accuracy of any conclusions made. Yet, it is obvious that the addition of two spacer groups lowers the clearing temperatures considerably for the series *2*; a trend also observed in the reverse series *1*. The large melting temperature lowering observed in the reverse esters *1* was, however, not observed in the esters *2*. Crystallization temperatures were always above room temperature. Clearing temperatures for the esters *1* (n = 2) are lower than those for the esters *2* (n = 2) even in the R′ = C_9 series when its higher clearing temperatures are used for comparison.§

§ The argument can be made that comparisons using an odd and an even R′ group is a poor one due to the odd-even alternation effect. However, the clearing temperature for the series *1* (n = 2) with R′ = C_8 should not be higher than that with R′ = C_9 since with the long R chains, these clearing temperatures are on the rising part of the clearing temperature curve in homologous series plots of phenylbenzoates.

TABLE I

Transition Temperatures (°C) for



X	Y	K [a]	B	C	A	N	I
C_{10}	CH_2OCOC_8	32.6					49.3-50.1
$C_{10}O$	CH_2OCOC_8	42.3					53.6-54.5
C_6O	$(CH_2)_2OCOC_8$	40.6 [b]					53.8-56.0
C_8O		35.7			(37.6)	(40.0)	56.7-57.2
$C_{10}O$		38.5	(40.1-40.6) [c]	(48.3-49.4) [c]	---	---	62.7-63.5
$C_{12}O$		28.6	(55.1-55.6) [c]	---	---	---	60.4-62.4
$C_{10}O$	$O(CH_2)_2OCOC_7$	51.5					61.9-62.6

[a] Crystallization temperature obtained using a cooling rate of 2°/min.
[b] $K_2 \rightarrow K_1$ at 42.1–52.0° on heating.
[c] These phases are near the crystallization temperature and were not always observed or they were seen simultaneously with slow-growing crystals.

The acyloxy series *2* (n = 0) shows a greater tendency to form S_C and S_B phases than the carboxylate series *1* (n = 0). Interestingly, this trend continues even when the chain ester is moved away from the benzene ring (n = 2) (Figure 1). The acyloxy series *2* (n = 2) shows a switch from a S_A-N to a S_C-S_B combination when the chain length of R increases from C_8 to C_{10}, but the carboxylate series *1* shows only N and S_A phases. As was true in the series *3*, no mesophases were observed when an oxygen atom was inserted between the benzene ring and the chain in series *4*.

Both the aldehydes *17* showed nematic and smectic A phases along with more than one crystalline form (Scheme V). The aldehyde with X = $C_{10}O$ was reported earlier to have a nematic and an unidentified smectic phase.[5] In both aldehydes, the smectic A phase was monotropic but whether the nematic phase was monotropic or enantiotropic or even seen at all, depended on which crystal form was involved in the melting transition. In both compounds, K_1 represents the most stable form; the one obtained when the crystallized sample was allowed to set overnight. When X = C_{10}, K_2 was usually the first crystals formed which, when reheated, immediately melted to the nematic phase. However, sometimes K_3 formed simultaneously with K_2 or on reheating K_2. Undoubtedly, there is some interconversion between these crystalline forms as K_1 is eventually formed, but these were not further investigated. Although the alcohols *19* were not expected to show mesophases (hydrogen-bonding would give nonlinear structures), the transition temperatures were also determined for these esters to confirm this prediction. No mesophases were observed. Melting temperatures were higher than for the aldehydes and the amount of supercooling was small giving little room for observing mesophases.

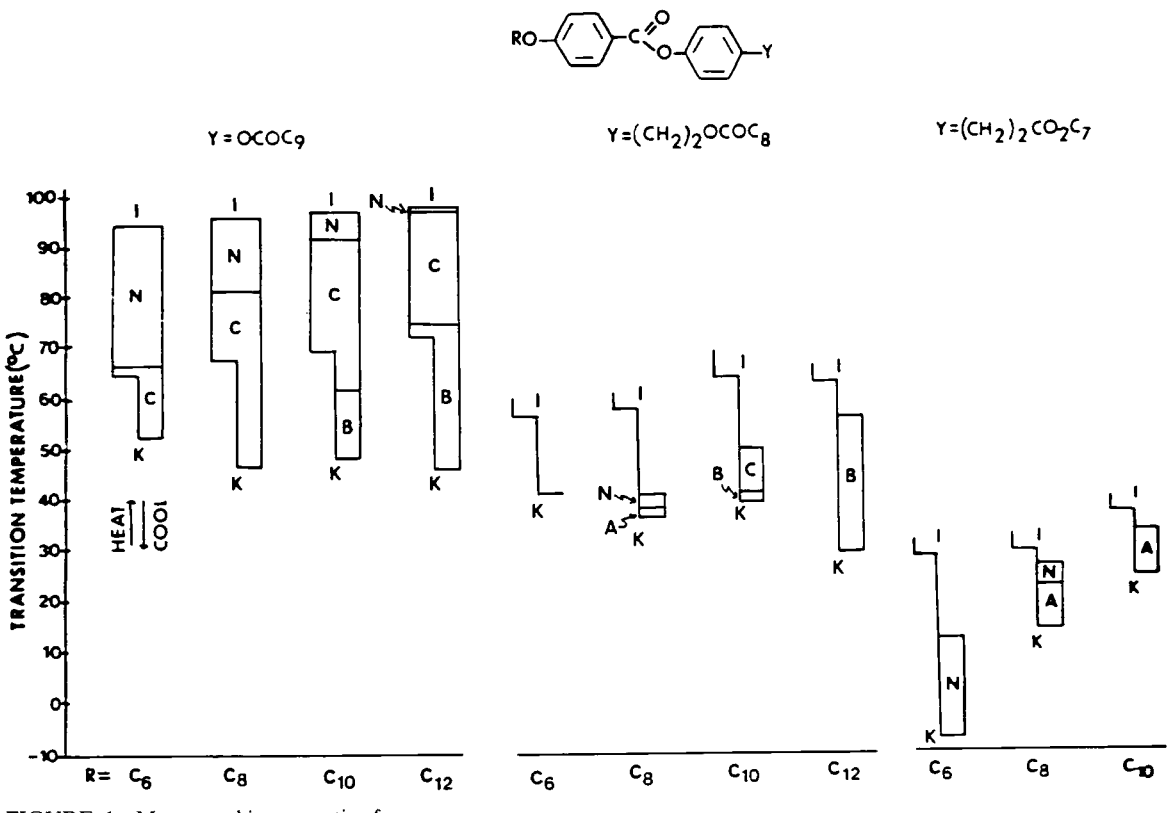
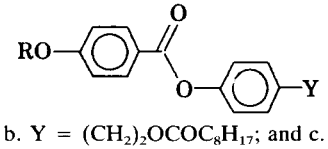
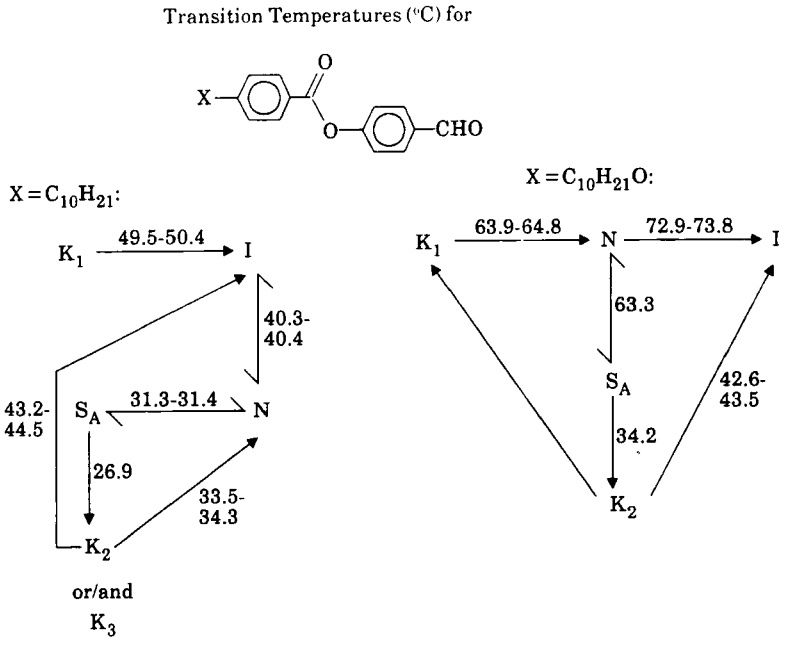


FIGURE 1 Mesomorphic properties for



a. Y = $OCOC_9H_{19}$, data from Reference 2; b. Y = $(CH_2)_2OCOC_8H_{17}$; and c. Y = $(CH_2)_2CO_2C_7$, data from Reference 1.

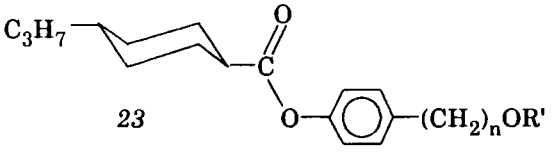


SCHEME V

DISCUSSION

When a terminal ester chain is attached directly to the benzene ring, it is not surprising that the mesomorphic properties differ considerably when this attachment is via the oxygen atom (*2*, n = 0) compared to when the attachment is through the carbon atom (*1*, n = 0) since electron conjugation is enhanced in the latter but not the former case. The addition of methylene spacer groups, however, eliminates this difference making it difficult to explain the differences in mesomorphic properties for the series *1* and *2* with n = 2 using only electronic consideration. The addition of spacer groups also eliminates any steric hindrance between the ester group and the aromatic ortho protons. This leaves for consideration only how the chains pack and their flexibility. The higher transition temperatures for the esters *2* (n = 2) than for the reverse esters *1* (n = 2) suggests less flexibility in the chains in series *2*.

It is interesting to note that a considerable lowering of the clearing temperatures was reported for the esters *23*.



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when n = 1 as compared with n = 0.[5] The clearing temperature curve for the

series with n = 1 does not show a regular odd-even alternation as does the curve when n = 0 supporting the idea that the chain with the spacer group is more flexible.

The comparison of mesomorphic properties for the ester series *1* and *2* with n = 2 with series *1* and *2* with n = 0 indicates that the mesophases in a series can be retained but transition temperatures changed by making small structural changes in the chains. This can be useful in "fine-tuning" the mesomorphic properties of these esters. Unfortunately, this modification tends to give shorter phase lengths and monotropic mesophases along with the lower temperatures.

EXPERIMENTAL

Anhydrous Na_2SO_4 was used to dry all organic extracts. The Pd/C catalysts were purchased from Strem Chemical Co. Melting points (°C) were determined using a Thomas-Hoover melting point apparatus and are corrected. Elemental analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

TLC data were obtained using Anal-Tech silica gel GHLF-Uniplates with UV light and I_2 as the detectors. All compounds were purified until they showed only one spot by TLC or a single component by HPLC (silica gel, Waters Prep 300 instrument). Flash chromatography was done using Aldrich grade 60 (mesh 230–400) silica gel.

IR spectra were run on a Pye-Unicam 3-200 instrument. NMR spectra were obtained using a Varian EM-360 instrument with TMS as an internal standard or on a General Electric GN300 (GN) instrument.

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 previously described.[7] Samples were cooled at 2°/min until they crystallized to obtain the crystallization temperature and so no monotropic mesophases occurring before this temperature were missed. Temperatures for monotropic phases (indicated by parentheses in the table) were obtained by immediately reheating these phases once formed. Mesophses were identified by the observance of known textures under crossed polarizers.[8,9] Conoscopic studies were done to determine whether smectic phases were uniaxial or biaxial. Abbreviations used are K = crystal, N = nematic, I = isotropic liquid and B, C and A indicate identified smectic phases with these designations.

4-Benzyloxybenzaldehyde

To a stirred mixture of 4-hydroxybenzaldehyde (48.8g, 0.40 mole), KOH (29.4g, 0.52 mole) and KI (500 mg) in a mixture of 600 ml EtOH and 100 ml H_2O was added dropwise benzyl chloride (56.8g, 0.45 mole). After refluxing for 48 hr, the reaction mixture was cooled, filtered and the filtrate rotovaped. The residue was dissolved in Et_2O (500 ml), washed with 5% aq KOH (2 × 200 ml), H_2O (2 × 200 ml), dried and filtered. The filtrate was rotovaped to give 72.0g (84.9%) of an oil. This oil was recrystallized from Et_2O (200 ml) to give 59.2g (69.8%) of 4-

benzyloxybenzaldehyde: mp 72–72° (lit.[10] mp 72°) and TLC ($CHCl_3$) R_f = 0.70, starting phenol R_f = 0.05).

4-Benzyloxybenzyl alcohol, 6 (n = 1)

This alcohol is now commercially available but it can be prepared by reduction of either the aldehyde or the acid:

Sodium borohydride (2.1g, 55.0 mmole) was added within 10 min to a stirred solution of 4-benzyloxybenzaldehyde (42.2g, 0.20 mole) in MeOH (300 ml) at 0°. Stirring was continued at RT for 1 hr and then the mixture rotovaped. Water (200 ml) was added to the residue and the mixture acidified with 2N HCl and extracted with Et_2O (400 ml). The Et_2O layer was washed with H_2O, dried, filtered and the solvent rotovaped from the filtrate to give an oil (40.5g, 94.6%). This material was recrystallized from Et_2O-hexane to give 32.1g (75.0%) of the purified alcohol *6*: mp 86° (lit.[11] mp 86–87°).

A solution of BH_3 in THF (125 ml, 1 molar) was added dropwise within 3 min to a stirred cooled (<10°) soln of 4-benzyloxybenzoic acid (25.0g, 0.11 mole) in THF (80 ml) under N_2. Stirring was continued for 16 hr as the temperature gradually rose to RT. This was again cooled to <0°, H_2O (50 ml) slowly added followed by K_2CO_3 (25.0g). The aqueous layer was separated and extracted with Et_2O (3 × 50 ml). This extract was combined with the original organic layer and washed with 10% aq KOH, satd NaCl and H_2O. The organic layer was dried, filtered and the filtrate rotovaped to give a colorless solid (22.5g, 96.4%): mp 84–87° and TLC ($CHCl_3$), R_f = 0.20 (starting acid R_f = 0.05).

4-Methoxycarbonyloxybenzaldehyde, *11*

To a cooled (−10°) stirred solution of 4-hydroxybenzaldehyde (36.6g, 0.30 mole), NaOH (12.0g, 0.30 mole) in H_2O (500 ml) was added dropwise (15 min) methyl chloroformate (29.2g, 0.31 mole). Stirring was continued at −10° for 30 min. The resulting precipitate was removed by filtration, washed with H_2O and dissolved in Et_2O (300 ml). This soln was washed with H_2O (100 ml), dried, filtered and the filtrate rotovaped to give 52.0g (96.2%) of a dark brown oil. Filtration of this oil through a short column of silica gel (100g) removed colored impurities to give 48.5g (89.8% of the purified aldehyde *11*: TLC ($CHCl_3$), R_f = 0.7 (starting phenol R_f = 0.05); IR ($CHCl_3$), 2840 and 2740 (wk, CHO), 1760 (str, OCO_2Me), 1700 (str, CHO) and 1600 cm^{-1} (str, Ar) and NMR ($CDCl_3$) δ10.15 (s, 1, CHO), 8.04 (d, J = 9.0 Hz, 2, ArH ortho to CHO), 7.45 (d, J = 9.0 Hz, 2, ArH ortho to OCO) and 3.98 (s, 3, CH_3).

4-Methoxycarbonyloxybenzyl Alcohol, *13*

Sodium borohydride (1.43g, 37.5 mmole) was added within 15 min to a stirred ice-cooled solution of the aldehyde *11* (27.0g, 0.15 mole) in MeOH (150 ml). Stirring was continued at 0° for 30 min. This mixture was then rotovaped, H_2O added (200 ml) and extracted with Et_2O (2 × 250 ml). The Et_2O layer was washed with H_2O, dried, filtered and the filtrate rotovaped to give 20.7g (75.8%) of an oil. Filtration of a solution of this material in 2% EtOH in $CHCl_3$ through a short column of 50g

silica gel gave 18.4g (67.4%) of the purified alcohol *13*: TLC ($CHCl_3$) R_f = 0.20 (starting aldehyde R_f = 0.80), IR ($CHCl_3$) 3600 and 3450 (wk, OH), 1740 (str, OCO_2Me), and 1590 cm^{-1} (wk, Ar) and NMR ($CDCl_3$) δ7.45 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 7.21 (d, J = 9.0 Hz, ArH ortho to OCO), 4.61 (s, 2, CH_2) and 3.91 (s, 3, CH_3).

β-(4-Benzyloxy)benzyl nonanoate, *10*, (n = 1)

Nonanoyl chloride (26.4g, 0.15 mole) was added dropwise to a stirred, cooled (0°) soln of the alcohol *6* (32.0g, 0.15 mole) and Et_3N (30.3g, 0.30 mole) in dry CH_2Cl_2 (200 ml). This mixture was allowed to warm to RT and stirred for 30 min. It was then washed with H_2O (2 × 100 ml), 1N HCl (2 × 100 ml), satd NaCl soln (100 ml) and H_2O (2 × 100 ml). The organic layer was dried, filtered and the filtrate rotovaped to give 42.4g (79.8%) of an oil which crystallized on standing: mp 40–41°, TLC (8% EtOAc in hexane), R_f = 0.31 (starting alcohol *6* R_f = 0), IR ($CHCl_3$) 1700 (OCOR) and 1600, 1580 cm^{-1} (med, Ar) and NMR ($CDCl_3$) δ7.48 (s, 5, C_6H_5), 7.38 (d, J = 8.0 Hz, 2, ArH ortho to CH_2), 7.01 (d, J = 8.0 Hz, 2, ArH ortho to OBz), 5.09 (s, 4, $2OCH_2$), 2.33 (t, J = 6.0 Hz, 2, $COCH_2$) and 2.10–0.40 (m, 15, C_7H_{15}).

(4-Methoxycarbonyl)benzyl nonanoate, *12*

This ester (a liquid) was prepared in the same manner as the benzyloxy derivative *10* in a yield of 29.3g (91.0%): TLC (8% EtOAc in hexane) R_f = 0.34 (starting alcohol R_f = 0), IR ($CHCl_3$) 1750 (str, $MeOCO_2$), 1730 (str, CO_2R), and 1600 cm^{-1} (wk, Ar) and NMR ($CDCl_3$) δ7.48 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 7.15 (d, J = 9.0 Hz, 2, ArH ortho to OCO), 5.06 (s, 2, $ArCH_2$), 3.83 (s, 3, CH_3), 2.30 (t, J = 6.0 Hz, 2, $COCH_2$) and 2.00–0.66 (m, 15, C_7H_{15}).

4-(4′-Decyloxybenzoyloxy)benzaldehyde, *17* (X = $C_{10}H_{21}O$)

This compound was synthesized by esterification of 4-decyloxybenzoic acid with 4-hydroxybenzaldehyde using the carbodiimide procedure as described earlier[2] in a crude yield of 95.5%. Recrystallization of this material from abs EtOH (3×) gave 2.8g (73.6%) of the purified aldehyde *17*: TLC ($CHCl_3$) R_f = 0.46 (4-hydroxybenzaldehyde, R_f = 0.14); IR (Nujol) 1730 (str, CO_2R), 1690 (str, CHO) and 1610 cm^{-1} (str, Ar) and NMR ($CDCl_3$, GN) δ10.01 (s, 1, CHO), 8.13 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R'), 7.95 (d, J = 8.7 Hz, 2, ArH ortho to CHO), 7.39 (d, J = 8.1 Hz, 2, ArH ortho to OCO), 6.98 (d, J = 8.7 Hz, 2, ArH ortho to OR), 4.04 (t, J = 6.3 Hz, 2, OCH_2), 1.82 (m, 2, $OCH_2\underline{CH_2}$), 1.48–1.28 (m, 14, $7CH_2$), and 0.88 (t, J = 6.0 Hz, 3, CH_3).

4-(4′-Decyloxybenzoyloxy)phenylmethanol, *19* (X = $C_{10}H_{21}O$)

Hydrogenation of a mixture of 2.6g (6.8 mmoles) of the aldehyde *17* (X = $C_{10}H_{21}O$) and 10% Pd-C (250 mg) in abs EtOH (40 ml) at 40 psi for 3 hr gave 2.5g (97.3%) of the crude product. Recrystallization of this material from Et_2O-hexane gave 2.1g (80.5%) of the purified alcohol *19* (X = $C_{10}H_{21}O$): TLC (2% EtOH in $CHCl_3$)

R_f = 0.26 (starting aldehyde, R_f = 1.0), IR (Nujol) 3500 (str, CO_2R) 3340 (med, br, OH), and 1600 cm^{-1} (str, Ar) and transition temperatures 84.2–85.0° (C-I) and 81.3° (I-C).

4-(4′-Decylbenzoyloxy)phenylmethanol, *19* (X = $C_{10}H_{21}$)

This alcohol was prepared in the same manner in a purified (Et_2O-hexane) yield of 73.8%: TLC (4% EtOH in $CHCl_3$) R_f = 0.47 (starting aldehyde R_f = 1.0), IR (Nujol) 3330 (med, br, OH), 1735 (str, CO_2R) and 1600 cm^{-1} (str, Ar); NMR ($CDCl_3$, GN) δ8.09 (d, J = 8.6 Hz, 2, ArH ortho to CO_2R), 7.52 (d, J = 9.0 Hz, 2, ArH ortho to CH_2O), 7.35 (d, J = 8.5 Hz, 2, ArH ortho to OCO), 7.29 (d, J = 8.1 Hz, 2, ArH ortho to CH_2R), 4.61 (s, 2, CH_2O), 2.68 (t, J = 7.5 Hz, 2, $ArCH_2$), 2.60 (s, 1, OH), 1.64 (t, J = 6.2 Hz, 2, $OCH_2\underline{CH_2}$); 1.31–1.26 (m, 14, $7CH_2$) and 0.88 (t, J = 5.7 Hz, 3, CH_3), and transition temperatures 82.8–83.3° (C-I) and 79.9° (I-C). NMR for the corresponding aldehyde *17* ($CDCl_3$, GN): δ10.02 (s, 1, CHO), 8.10 (d, J = 7.8 Hz, 2, ArH ortho to CO_2R), 7.96 (d, J = 6.9 Hz, 2, ArH ortho to CHO), 7.40 (d, J = 8.7 Hz, 2, ArH ortho to OCO), 7.32 (d, J = 7.5 Hz, 2, ArH ortho to CH_2), 2.70 (t, J = 6.0 Hz, 2, $ArCH_2$), 1.65 (t, J = 6.0 Hz, 2, $ArCH_2\underline{CH_2}$), 1.32–1.31 (m, 14, $7CH_2$) and 0.88 (t, J = 6.0 Hz, 3, CH_3).

β-(4-Benzyloxy)phenylethylalcohol, *6* (n = 2)

Method 1: The acid *5* (n = 1)* was treated with BH_3 as described for the synthesis of the alcohol *6* (n = 1) to give a 92.7% yield of the crude alcohol *6* (n = 2): mp 84.0–86.5°, TLC ($CHCl_3$) R_f = 0.44 (starting acid, R_f = 0.17) and IR ($CHCl_3$) 3375 (str, OH), 1580 cm^{-1} (str, Ar) and no C = 0 absorption. This material was esterified without further purification.

Method 2: The acid *5* (n = 2)‖ was converted to the acid chloride *7* using PCl_5. The $POCl_3$ was removed *in vacuo* and the residue dissolved in 200 ml dry CH_2Cl_2. This solution was added dropwise within 30 min to a stirred solution of Et_3N (26.4 ml, 0.19 mole), MeOH (6.1 ml) in 20 ml CH_2Cl_2 at 0°. The reaction mixture was stirred for 17 hr at RT and then refluxed for 1 hr.¶ The cooled reaction mixture was washed with H_2O (2×), 5% aq KOH and H_2O. The organic layer was dried, filtered and the filtrate rotovaped to give 42.4g (87.1%) of the crude methyl ester *8*. Recrystallization of this material from MeOH gave 32.2g (66.1%) of the purified ester *8*: mp = 56–59° TLC ($CHCl_3$) R_f = 0.59 (R_f of the acid *5*, (n = 1) R_f = 0.13); and IR (Nujol) 1720 (str, CO_2R), 1620, 1600 cm^{-1} (med, Ar) and no acid C = 0 peaks.

A solution of this ester (32.2g, 0.13 mole) in Et_2O was added dropwise to a stirred suspension of LAH (9.6g, 0.25 mole) in Et_2O at RT. The reaction mixture was refluxed for 21 hr, slowly poured into a mixture of concd HCl (75 ml) and crushed ice (500g) and stirred overnight. The resulting precipitate was collected

‖ For the synthesis of this acid, see Reference 1.
¶ Just refluxing for 1 hr should be sufficient.

by filtration, washed well with H_2O and dried. This material was dissolved in $CHCl_3$, filtered through Celite and the filtrate rotovaped to give 26.0g (90.3%) of colorless crystals of the alcohol *6* (n = 2): mp 85.5–87.0°; TLC ($CHCl_3$) R_f = 0.27 (R_f for the ester *8*, 0.52); IR (Nujol) 3200–3000 (str, OH) and 1610, 1590 cm^{-1} (med, Ar), and NMR ($CDCl_3$) δ7.30 (s, 5, C_6H_5), 7.09 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 6.84 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.94 (s, 2, $ArOCH_2$), 3.68 (t, J = 7.0 Hz, 2, CH_2OH), 2.68 (t, J = 6.0 Hz, 2, $ArCH_2$) and 1.93 (s, 1, OH). This material was esterified without further purification.

β-(4-Benzyloxy)phenylethyl nonanoate, *10* (n = 2)

This ester was prepared by esterification of the alcohol *6* using the standard acid chloride/Et_3N method[2] and recrystallized from abs EtOH to give colorless crystals: mp 51–53°; TLC R_f = 0.88 (alcohol *6*, (n = 2) R_f = 0.26); IR 1720 (str, CO_2R) and 1600, 1560 cm^{-1} (wk, Ar) and NMR ($CDCl_3$) δ7.29 (s, 5, C_6H_5), 7.05 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 6.78 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.95 (s, 2, $ArCH_2O$), 4.13 (t, J = 7.0 Hz, 2, CH_2OCO), 2.78 (t, J = 7.0 Hz, 2, $ArCH_2$), 2.17 (t, J = 6.0 Hz, 2, $COCH_2$) and 1.90–0.60 (m, 15, C_7H_{15}).

β-(4-Hydroxy)phenylethyl nonanoate, *9* (n = 2)

A soln of the ester *10* (n = 2) (10.3g, 28.2 mmole) in abs EtOH (120 ml) (with heating) containing 3.0g 5% Pd-C was hydrogenated at 54 lbs/in^2 and 30° for 1 hr. The catalyst was removed by filtration through Celite on hardened (no. 50) filter paper and the filtrate rotovaped to give 7.76g (99.2%) of the crude phenol *9*. This material was passed through a silica gel column (50g, 60–100 mesh) using 1:1 THF-hexane as the eluting solvent to give 7.55g (96.5%) of the liquid phenol *9*. It could also be purified by flash chromatography on silica gel using CH_2Cl_2 as the eluting solvent (85.5%). TLC ($CHCl_3$) R_f = 0.24 (starting ester *10*, R_f = 8.5) and IR (film) 3600–3200 (br, med, OH), 1720 (str, CO_2R) and 1600 cm^{-1} (med, Ar), and NMR ($CDCl_3$) 7.05 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 6.79 (d, J = 9.0 Hz, 2, ArH ortho O), 5.94 (s, 1, OH), 4.24 (t, J = 7.0 Hz, 2, CH_2OCO), 2.81 (t, J = 7.0 Hz, 2, $ArCH_2$), 2.28 (t, J = 6.0 Hz, 2, CH_2CO_2), and 1.90–0.50 (m, 17, C_8H_{17}). *Anal.* calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.42. Found: C, 73.15; H, 9.22.

2-Bromoethyl octanoate, *21*

This ester was prepared using the method described for ester *6* (n = 1) in a crude yield of 95.8%. Distillation at 150–155° (0.6 mm) gave 42.8g (84.9%) of the bromoester *21*: TLC (8% EtOAc in hexane) R_f = 0.45 and IR (film) 1720 cm^{-1} (str, CO_2R).

β-(4-Benzyloxyphenoxy)ethyl octanoate, *23*

The bromoester *21* (12.6g, 0.05 mole) was added dropwise to a stirred solution of 4-benzyloxyphenol (10.0g, 0.50 mole) and anhyd K_2CO_3 (14.0g, 0.10 mole) in dry acetone (200 ml). The reaction mixture was refluxed for 72 hr, filtered and the filtrate rotovaped to give 17.5g (94.6%) of a dark brown oil. This material was

filtered through a column of silica gel (100g) using 5% EtOAc in hexane as the eluting solvent and then recrystallized from abs EtOH to give 10.7g (57.8%) of the purified ester *23*: mp 59.5–61.0°, TLC (8% EtOAc in hexane) R_f = 0.24 (starting phenol R_f = 0.5 and ester *21*, R_f = 0.45); IR ($CHCl_3$), 1720 (str, CO_2R) and 1580 cm^{-1} (wk, Ar), and NMR ($CDCl_3$, GN) δ7.42–7.30 (m, 5, C_6H_5), 6.91–6.82 (m, 4, ArH), 4.99 (s, 2, $C_6H_5\underline{CH_2}$), 4.38 (t, J = 4.24 Hz, 2, CH_2OCO), 4.10 (t, J = 3.76 Hz, 2, $ArOCH_2$), 2.33 (t, J = 7.7 2Hz, 2, $COCH_2$), 1.62 (t, J = 6.98 Hz, 2, $COCH_2\underline{CH_2}$), 1.28 (m, 8, $4CH_2$), and 0.87 (t, J = 5.64 Hz, 3, CH_3).

β-(4-Hydroxyphenoxy)ethyl octanoate, 22

This phenol was prepared by hydrogenation of the ester *23* in the same manner as described for the phenol *9* to give 9.5g (95.2%) of a liquid which solidified on standing: mp 35.0–37.0°, TLC (4% EtOH-$CHCl_3$), R_f = 0.41 (starting ether R_f = 0.7); IR ($CHCl_3$) 3420 (str br, OH), 1720 (str, CO_2R) and 1600 cm^{-1} (v wk, Ar), and NMR ($CDCl_3$, GN) 6.78 (s, 4, ArH), 5.68 (s, 1, OH), 4.40 (3 peaks, J = 5.60 and 3.75, 2, CH_2OCO), 4.10 (t, J = 4.67 Hz, 2, $ArOCH_2$), 2.35 (t, J = 7.44, 2, $COCH_2$), 1.63 (t, J = 6.54, 2, $COCH_2\underline{CH_2}$), 1.27 (s, 8, $4CH_2$), and 0.87 (t, J = 6.10 Hz, 3, CH_3). *Anal.* calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.71; H, 8.65.

Typical NMR spectral data for the esters *2* and *4* are as follows: *2* (X = $C_{10}H_{21}$, Y = $CH_2OCOC_8H_{17}$) (CCl_4) δ8.10 (d, J = 9.0 Hz, 2, ArH ortho to CO_2), 7.39 (d, J = 9.0 Hz, 2, ArH ortho to CH_2OCO), 7.25 (d, J = 9.0 Hz, 2, ArH ortho CH_2R), 7.18 (d, J = 9.0 Hz, 2, ArH ortho to O), 5.06 (s, 2, CH_2O), 2.66 (t, 2, J = 7.0 Hz, 2, $ArCH_2$), 2.27 (t, J = 7.0 Hz, 2, $COCH_2$), and 2.00–0.66 (m, 34, C_9H_{19}, C_7H_{15}); *2* (X = $C_{10}H_{21}O$, Y = $CH_2OCOC_8H_{17}$) (CCl_4), δ8.25 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.50 (d, J = 9.0 Hz, 2, ArH ortho to CH_2OCO), 7.25 (d, J = 9.0 Hz, 2, ArH ortho to OCO), 6.97 (d, J = 9.0 Hz, 2, ArH ortho to OR), 5.18 (s, 2, $ArCH_2O$), 4.08 (t, J = 6.0 Hz, 2, $ArOCH_2$), 2.40 (t, J = 7.0 Hz, 2, $COCH_2$), and 2.08–0.65 (m, 34, C_9H_{19}, C_7H_{15}); *2* (X = $C_6H_{13}O$, Y = $(CH_2)_2OCOC_8H_{17}$) ($CDCl_3$) δ8.27 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.25 (s, 4, ArH ortho to OCO and CH_2), 6.99 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.32 (t, J = 7.0 Hz, 2, CH_2OCO), 4.03 (t, J = 6.0 Hz, 2, $ArOCH_2$), 2.95 (t, J = 7.0 Hz, 2, $ArCH_2$), 2.30 (t, J = 6.0 Hz, 2, $COCH_2$) and 2.00–0.60 (m, 26, C_5H_{11}, C_7H_{15}) and *4* (X = $C_{10}H_{21}O$ and Y = $O(CH_2)_2OCOC_7H_{15}$) (CCl_4) δ8.01 (d, J = 9.0 Hz, 2, ArH ortho to CO_2R), 7.01 (d, J = 9.0 Hz, 2, ArH ortho to OCO) 6.82, 6.79 (2d, J = 9.0 Hz, 4, ArH ortho to OCH_2), 4.45–3.72 (m, 6, $ArOCH_2$ and OCH_2CH_2), 2.33 (t, J = 7.0 Hz, 2, $COCH_2$) and 2.00–0.65 (m, 32, C_9H_{19}, C_6H_{13}).

Acknowledgment

This material is based on work partially supported by the National Science Foundation-Solid State Chemistry grants DMR83-09739, DMR85-5221 and DMR88-18561.

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