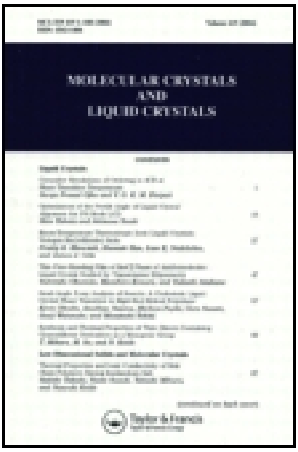

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The Effect of Carbonyl Containing Substituents in the Terminal Chains on Mesomorphic Properties in Some Aromatic Esters and Thioesters.6.Phenylbenzoates Containing a $(CH_2)_n$ COR′ Group (n = 1,2) on the Phenolic End

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The Effect of Carbonyl Containing Substituents in the Terminal Chains on Mesomorphic Properties in Some Aromatic Esters and Thioesters.6.Phenylbenzoates Containing a $(CH_2)_n$ COR′ Group (n = 1,2) on the Phenolic End†

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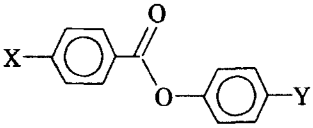
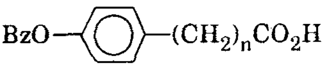
Substituted phenylbenzoates of the type



where X = R, RO; (Y = $(CH_2)_nCOR'$, n = 1, R′ = C_8H_{17} and n = 2, R′ = C_7H_{15} have been prepared to determine the effect of the spacer methylene groups on the mesomorphic properties of esters having a ketone chain on the phenolic side. The required precursor phenols were prepared by treatment of the protected acids



with an alkyllithium followed by hydrogenolysis of the benzyl group. The analogous cyclohexane diesters

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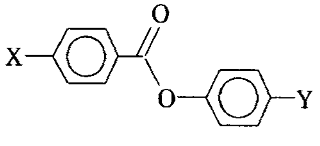
were also synthesized to test the generality of trends observed in mesomorphic properties. Hot stage polarizing microscopy was used to determine mesomorphic properties. These were compared to those for the esters with *Y* = $C_{10}H_{21}$,COR′ and $(CH_2)_nCO_2R'$ (*n* = 1,2).

INTRODUCTION

Earlier, we reported that the esters *1* with an α-keto



X = R, RO

1 COR'
2 $(CH_2)_nCO_2R'$, n = 0-2
3 $(CH_2)_nCOR'$
a n = 1, R' = C_8H_{17}
b n = 2, R' = C_7H_{15}

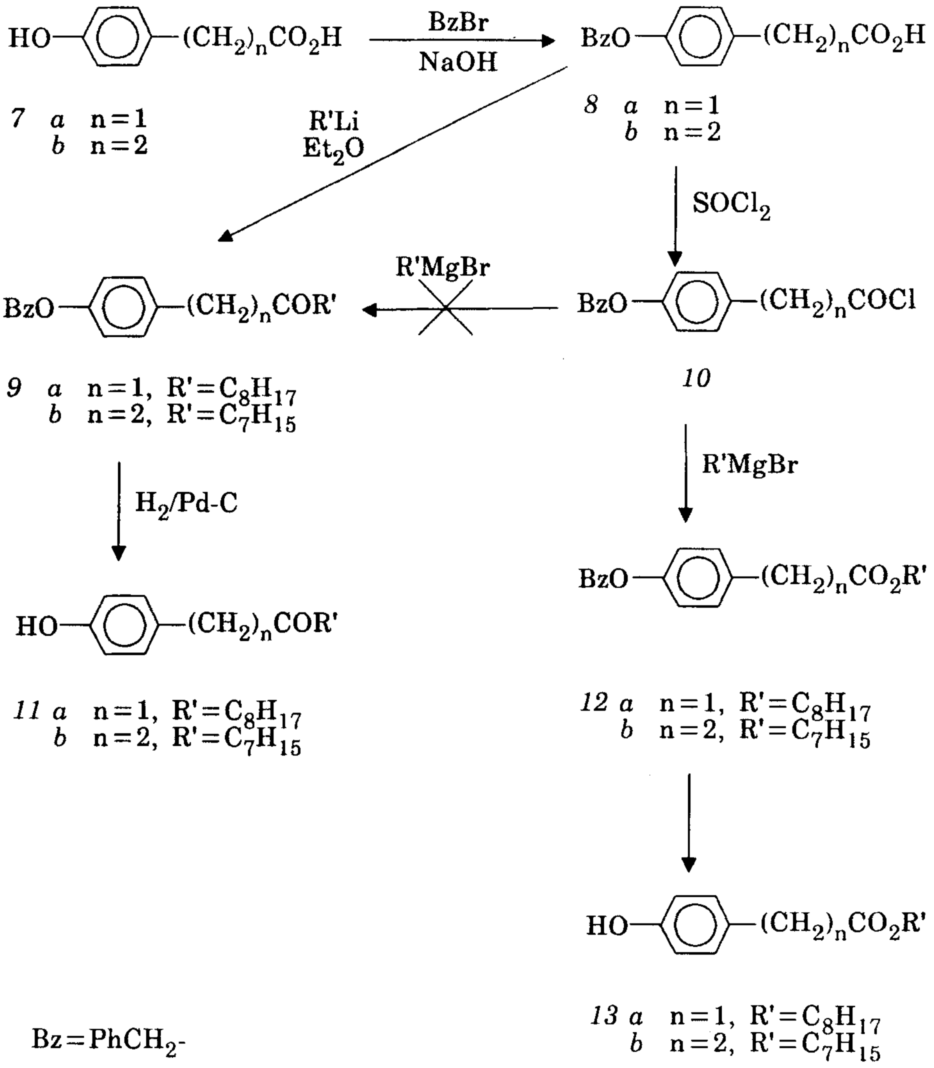
chain on the phenolic end show only smectic A phases with long chain lengths, although nematics are sometimes observed at shorter chain lengths.[1] However, this preference for the smectic A phase did not occur in the corresponding cyclohexane diesters *4* which show only nematic

4 COR'
5 $(CH_2)_nCO_2R'$, (n = 0-2)
6 $(CH_2)_nCOR'$, (n = 1-2)

and smectic C phases.[1] We have also determined the mesomorphic properties for the phenylbenzoates with an ester group incorporated into the phenolic chain *2* both with the ester attached directly to the ring (*n* = 0) and also with one and two spacer methylene groups (*n* = 1,2).[2] No mesophases were observed when *n* = 1. Both smectic A and C phases occurred when *n* = 0 but only smectic A phases when *n* = 2. Unlike the α-keto chain which causes an appreciable increase in transition temperatures, the CO_2R' chain created little variation from those observed for the *Y* = R′ series. Transition temperatures decreased with each additional spacer group and the mesophases observed were generally of shorter range and/or monotropic. We were interested in determining if this were also true in the keto chain esters containing spacer groups *3* and the corresponding cyclohexane diesters *6*. Since the α-keto esters *1* have smectic A phases of reasonable phase length but at high temperatures, we hoped that adding spacer groups to the keto chain would give enantiotropic smectic A phases of reasonable phase lengths at lower temperatures.

SYNTHESIS

Our first attempt to prepare the required keto phenols *11* via a Grignard reaction on the acid chloride *10*[3] gave instead the esters *12* (Scheme I). A number of the phenylbenzoates *2* and cyclohexane diesters *5* were prepared from the isolated phenols before it was realized that the ester, rather than the keto chain, had been isolated. Since data for several of these esters were available from our earlier work,[2] a comparison showed essentially identical transition temperatures. A closer scrutiny of the NMR spectra for the phenols showed the OCH_2 protons that would occur



SCHEME I

in the ester but not the keto chain. However, the cyclohexane diesters prepared from these phenols had lower melting temperatures than authentic samples (Table III) and small amounts of impurities were detected in the NMR spectra. Repeated recrystallizations increased the melting temperature of the ester *5* (n = 1) to 86.2–86.6°, still below that of the authentic sample but a mixture melting point showed no melting point depression (85.7–86.3°) confirming that both samples were the same compound. Since the most logical way the ester *12* could have formed is by reaction of the Grignard reagent with the acids *8*, attempts were made to obtain the desired ketones *9* by taking additional precautions to assure that anhydrous conditions were present. However, the ester *12* was still isolated as the predominant product. No ketone could be found. Several different catalysts (MnI_2,[4] $CdCl_2$[5] and $Ni(Ph_2PCH_2CH_2PPh_2Cl_2$[6]) for the Grignard reaction were also tried without success.

The desired ketones *9* were prepared by treating the acids *8* with an alkyl lithium reagent[7] rather than a Grignard reagent (Scheme I). Hydrogenolysis of the benzyl group gave the phenols *11*.

The phenols *11* were esterified with either a 4-alkyl or a 4-alkoxybenzoic acid or 1,4-*trans*-cyclohexane dicarboxylic acid using either the acid chloride/TEA or the carbodiimide method.[8] All compounds were purified using recrystallization and flash chromatography on silica gel until only one spot was observed by TLC (silica gel). Structures were confirmed by NMR and in some instances by elemental analysis. Typical examples of detailed synthesis procedures and characterization data are given in the experimental section.

MESOMORPHIC PROPERTIES

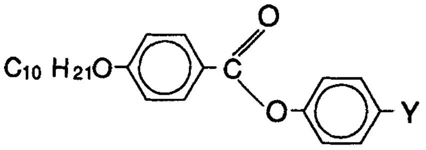
Mesomorphic properties (°C) for the keto chain esters *3* along with those for the esters chain esters *2* not reported earlier are presented in Tables I and II. Data for the analogous cyclohexane diesters *5* and *6* are given in Table III. Hot-stage polarizing microscopy was used to collect these data. Definitions for abbreviations and additional details are given in the experimental section.

A comparison of the melting temperatures for the keto chain esters *3* (X = $C_{10}H_{21}$) with those for the analogous ester chain, esters *2* (Table I) indicates that these temperatures are always higher for the keto than for the ester chains. With each additional spacer methylene group, the melting temperature falls; a trend observed in the ester chain esters as well. The decrease in temperature for one CH_2 group is larger in the ester chain (~27 vs 14) but comparable to that in the keto chain (~15 vs 13) when n = 2. Melting temperatures for the keto chains are also higher than when Y is an alkyl chain whereas this is not true for the ester chains when $n > 0$.

When X is an alkoxy chain (Table II), the melting temperatures are again higher for the keto than for the ester chains and decrease with each additional spacer methylene group as is true in the esters. However, the decrease when n = 2 is only a few degrees more than when n = 1 in the keto chain series. Interestingly, the decrease with n = 1 is much larger in the keto chain when X = OR (~41)

TABLE I

Melting Temperatures (°C) for



Y	M.P. (°C)
C_{10} [a]	52.0-53.5
COC_9 [b]	101.6-101.8
CH_2COC_8	87.2-87.5
$(CH_2)_2COC_7$	73.0-73.2
CO_2C_9 [c]	68.5-69.8
$CH_2CO_2C_8$	42.4-42.6
$(CH_2)_2CO_2C_7$ [c]	24.3-26.9

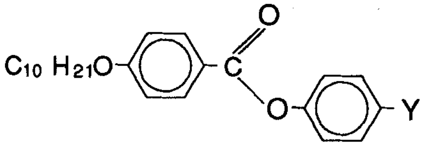
a. Data from reference 9.

b. Data from reference 1.

c. Data from reference 2.

TABLE II

Transition Temperatures (°C) for



Y	K	A	I
C_{10} [a]	46.1	61.2-61.9	74.6-75.5
COC_9 [b]	95.8	107.0-107.6	120.4-120.7
CH_2COC_8	72.4	- - -	78.2-78.5
$(CH_2)_2COC_7$	68.7	(70.5)	77.0-77.1
CO_2C_9 [c]	51.5	68.8-69.4	74.4-74.7
$CH_2CO_2C_8$	44.3	- - -	48.8-49.2
$(CH_2)_2CO_2C_7$ [c]	23.6	(32.3-32.5)	35.6-36.2

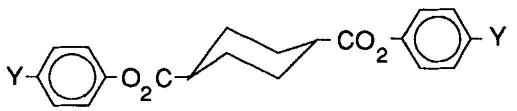
a. Data from reference 9.

b. Data from reference 1.

c. Data from reference 2.

TABLE III

Transition Temperatures (°C) for



Y	K	B	C	A	I
C_{10} [a]	51.2	64.8-65.7	- - -	117.2-117.7	134.6-135.2
COC_9 [b]	95.6	- - -	103.4-104.5	- - -	186.7-189.2
CH_2COC_8	124.2	- - -	- - -	- - -	128.4-129.2
$(CH_2)_2COC_7$	115.6	(123.5)	- - -	- - -	129.9-130.5
CO_2C_9 [c]	67.8	- - -	- - -	79.8-80.7	138.0-138.3
$CH_2CO_2C_8$	76.5	- - -	- - -	- - -	80.6-81.6[d]
$CH_2CO_2C_8$	84.3	- - -	- - -	- - -	90.9-91.4[e]
$(CH_2)_2CO_2C_7$	41.1	(60.8-61.8)	- - -	- - -	73.0-74.1[d]
$(CH_2)_2CO_2C_7$ [c]	46.8	(60.1-61.1)	- - -	- - -	76.0-76.9

a. Data from reference 10.
b. Data from reference 1.
c. Data from reference 2.
d. Material prepared using the phenol *13* isolated from the Grignard reaction. A higher melting temperature was obtained on further recrystallization (see text).
e. Material prepared using the phenol *13* prepared as in reference 2.

than when $X = R$ (~14). Again the melting temperatures for the keto chain esters are higher than the melting temperatures for the alkyl chain whereas the ester chain esters again show lower melting temperatures when $n > 0$.

Only a short range monotropic smectic A phase was observed in the keto chain series and only when $n = 2$ and $X = C_{10}H_{21}O$. No mesophases were observed when $X = C_{10}H_{21}$ or when $n = 1$. This same trend was also observed in the ester chain esters.

Most of these trends do not occur in the cyclohexane diester series *4* and *6* (Table III). The α-keto chain gives a higher melting temperature than the alkyl chain but the addition of spacer methylene groups produces even higher melting temperatures with little difference between those for $n = 1$ and $n = 2$. With an ester chain, the melting temperature is higher when $n = 1$ than when $n = 0$ but is lower when $n = 2$. A smectic C phase occurs when $n = 0$ in the keto chain whereas the usual S_A phase is present in the ester chain series. Again, no mesophases were observed when $n = 1$; the only consistent trend observed. Interestingly, smectic B, rather than smectic A, phases occur in both the keto and ester chain series when $n = 2$.

Certainly, the higher melting temperatures observed for all the keto chain esters than for the alkyl esters indicates that the dipole of the ketone group has a strong influence on the intermolecular forces. The lowering of the melting temperatures with the addition of spacer groups in the phenylbenzoates suggests that these chains have more flexibility whereas the increased temperatures in the cyclohexane diester series suggest that these keto chains are more rigid or perhaps the ketone dipole overrides the chain flexibility in determining the melting temperatures.

EXPERIMENTAL

The acid *7b* was prepared by hydrogenation of 4-hydroxycinnamic acid in a yield of 99.0% as described earlier.[2] Synthesis of 4-nonanoyloxybenzoic acid was achieved using the previously reported method.[11] The 4-alkoxybenzoic acids, 1,4-*trans*-cyclohexane dicarboxylic acid and 4-hydroxyphenylacetic acid are all commercially available. The Pd catalyst was obtained from Strem Laboratories.

Anhydrous Na_2SO_4 was used to dry all organic extracts unless otherwise stated. TLC data were obtained using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as detectors. All compounds were purified first by column chromatography on silica gel (60–100 mesh) and then recrystallized until they showed only one spot by TLC. Melting points were determined using a Thomas-Hoover melting point apparatus and are corrected. The elemental and mass spectral analyses were obtained from Oneida Research Services, Inc., Whitesboro, NY.

IR spectra were run on a Pye-Unicam 3-200 instrument and NMR spectra obtained in $CDCl_3$ using either a Varian FT80 (FT) or a General Electric GN-300 (GN) instrument with TMS as the internal standard. The published NMR spectra for 1-phenyl-2-butanone,[12] the 4,4′-disubstituted phenylbenzoates[13] and the esters *2*[2] were used to assist in peak identification.

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.[14] Samples were cooled at 2°/min until they crystallized to obtain the crystallization temperature and so no monotropic phases occurring below this temperature were missed. Abbreviations used for phases are K = crystal, N = nematic and B, C, and A indicate identified smectic phases. Mesophases were identified by the observance of known textures[15,16] and conoscopic studies used to determine whether smectic phases were uniaxial or biaxial.

Octyl-4-benzyloxyphenyl Acetate, *12a*

A solution of octyl magnesium bromide was prepared by treating a stirred solution of 1-bromo-octane (16.0 g, 82.6 mmole) in anhyd Et_2O (100 ml) with 2.2 g Mg. The Et_2O was removed and replaced with anhyd THF (100 ml) and the resulting solution added dropwise under N_2 within 30 min to a stirred solution of crude 4-benzyloxyphenylacetyl chloride [prepared from 20.0 g (82.6 mole) of the acid using $SOCl_2$] and ferric acetyl acetonate (880 mg, 2.48 mmole) in THF (800 ml) at RT. Stirring was continued for 24 hr, 10% HCl added to quench the reaction and the mixture extracted with Et_2O. The Et_2O layer was washed with satd $NaHCO_3$ solution and H_2O, dried and filtered. The solvent was rotovaped from the filtrate and the residue extracted with hot petroleum ether (3 ×). Removal of the solvent

(Rotovap) and chromatography of the residue on silica gel gave 18.6 g (66.6%) of the ester *12a* using CH_2Cl_2 as the eluting solvent. However, TLC ($CHCl_3$) showed two spots with R_f = 0.63 and 0.71. Distillation at 130° (0.3 mm) removed some low boiling impurities to give the purified ester *12a*: TLC ($CHCl_3$) R_f = 0.63 (R_f = 0.03 for starting acid *8a*); IR (film) 1740 (str CO_2R) and 1615, 1590 cm^{-1} (med, wk Ar) and NMR (GN) δ7.40–7.26 (m, 5, C_6H_5), 7.17 (d, J = 6.7 Hz, 2, ArH ortho to CH_2), 6.91 (d, J = 7.9 Hz, 2, ArH ortho to O), 5.00 (s, 2, $OCH_2C_6H_5$), 4.06 (q, J = 5.9 Hz, 2, CO_2CH_2), 3.52 (s, 2, $ArCH_2CO$), 1.78 (q, J = 6.5 Hz, 2, $CO_2CH_2\underline{CH_2}$), 1.58 (t, J = 4.4 Hz, 2, $CO_2CH_2CH_2\underline{CH_2}$), 1.26 (m, 8, $4CH_2$) and 0.88 (s, 3, Me).

The ester *12b* was formed in the same manner from the acid *8b*. However, it was not obtained pure although chromatographed (2 × flash) on silica gel by eluting with hexane-EtOAc (9:1) in a yield of ca. 24.7%. NMR (FT) showed a triplet at 3.50δ and a more complicated multiplet at 3.30–2.80δ than shown by the ester along with the CO_2CH_2 triplet at 4.00δ and no $COCH_2$ peak. Additionally, the aliphatic integral was considerably less than expected. This material, however, did form some of the ester *2* when converted to the phenol *13b* and esterified suggesting that some of the ester *12b* was present.

4-Benzyloxy-2′-oxo-decylbenzene, *9a*

To a stirred suspension of freshly cut Li wire (1.4 g, 0.20 mole) in anhyd Et_2O (35 ml) under N_2 at 0–5° was added dropwise (4.5 hr) a solution of 1-bromooctane (19.5 g, 0.10 mole) in 35 ml anhyd Et_2O. The reaction mixture was allowed to warm to 10° over a period of 2 hr and then added dropwise to a stirred solution of the acid *8a* (9.4 g, 39.0 mmole) in Et_2O (700 ml) under N_2 at 0°. The reaction mixture was refluxed for 24 hr, cooled to RT and H_2O (200 ml) carefully added. The Et_2O layer was separated, combined with a second extract, washed with H_2O, dried (anhyd $MgSO_4$) and filtered. The filtrate was rotovaped and the residue purified by column chromatography on silica gel (60–100 mesh). Elution with CH_2Cl_2-hexane (3:1) gave 2.6 g (19.7%) of the ketone *11a*: TLC (3:1 CH_2Cl_2-hexane) showed one spot with R_f = 0.48 (R_f for starting acid *8a* = 0.0); IR (Nujol) 1720 (str, C=O) and 1615, 1520 cm^{-1} (med, Ar) and NMR (FT) δ7.35 (s, 5, C_6H_5), 7.08 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 6.83 (d, J = 9.0 Hz, 2, ArH ortho to O), 5.00 (s, 2, $OCH_2C_6H_5$), 3.55 (s, 2, $ArCH_2CO$), 2.38 (t, J = 7.0 Hz, 2, $COCH_2C_7$), 1.65–1.05 (m, 12, $6CH_2$) and 0.87 (t, J = 6.0 Hz, 3, CH_3).

4-Benzyloxy-3′-oxodecylbenzene, *9b*

This compound was prepared in the same manner as described for the ketone *9a* except that the bromide was added within 30 min to the Li suspension and the alkyl lithium added to the acid *8b* solution at RT. The crude product was chromatographed on silica gel using EtOAc-hexane (2.5%) as the eluting solvent to give 10.0 g (75.6%) of the purified ketone *11b*: TLC (5% EtOAc-hexane) R_f = 0.29 (R_f for starting acid *8b* = 0.0); IR (Nujol) 1685 (str, C=O) and 1595 cm^{-1} (wk, Ar) and NMR (FT) δ7.28 (m, 5, C_6H_5), 7.02 (d, J = 9.0 Hz, ArH ortho to

CH_2), 6.82 (d, J = 9.0 Hz, 2, ArH ortho to O), 4.95 (s, 2, $OCH_2C_6H_5$), 2.79 (t, J = 7.0 Hz, 2 $ArCH_2$), 2.69 (t, J = 7.0 Hz, 2, CH_2COC_6), 2.32 (t, J = 7.0 Hz, 2, $CH_2CO\underline{CH_2}C_6$) and 1.90–0.68 (m, 13, C_6H_{13}).

4-Hydroxy-2′-oxodecylbenzene, *11a*

A solution of the benzyl ether *9a* (3.5 g, 10.4 mmole) in EtOAc (100 ml) containing 5% Pd-C (500 mg) was hydrogenated at 50 psi and 50° for 24 hr. The catalyst was removed from filtration through Celite and the filtrate rotovaped to give 2.57 g (quant) of the crude phenol *11a*: TLC (5% EtOAc-hexane) R_f = 0.06 (R_f for *4a* = 0.28); IR (Nujol) 3300 (med br, OH), 1720 (str, C═O) and 1610 cm^{-1} (wk, Ar) and NMR (FT) δ6.98 (d, J = 9.0 Hz, 2, ArH ortho to CH_2), 6.85 (s, 1, OH), 6.80 (d, J = 8.0 Hz, 2, ArH ortho to OH), 3.58 (s, 2, $ArCH_2CO$), 2.40 (t, J = 6.0 Hz, 2, $ArCH_2CO\underline{CH_2}$) and 1.60–0.60 (m, 15, C_7H_{15}). Elemental Analysis Calcd for $C_{16}H_{24}O_2$: 77.37% C, 9.74% H. Found: 77.26% C, 9.87% H.

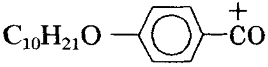
4-Hydroxy-3′-Oxodecylbenzene, *11b*

This compound was prepared in the same manner as the ketone *1a* in a quantitative crude yield: TLC (5% EtOAc-hexane) R_f = 0.0 (R_f for *4b* = 0.29), IR (Nujol) 3390 (med br, OH), 1690 (str, C═O) and 1600, 1585 cm^{-1} (wk, Ar) and NMR (GN) δ7.00 (d, J = 7.97 Hz, 2, ArH ortho to CH_2), 6.76 (d, J = 7.91 Hz, 2, ArH ortho to OH), 2.81 (t, J = 7.05 Hz, 2, $ArCH_2$), 2.70 (t, J = 7.25 Hz, 2, $ArCH_2\underline{CH_2}CO$), 2.38 (t, J = 7.25 Hz, 2, $COCH_2R$), 1.54 (m, 2, $COCH_2\underline{CH_2}$), 1.24 (s, 8, $4CH_2$) and 0.86 (s, 3, Me). Elemental Analysis Calcd for $C_{16}H_{24}O_2$: 77.37% C, 9.74% H. Found: 77.49% C, 9.63% H.

The esters *2*, *3*, *5* and *6* were prepared by esterification of the appropriate phenol with a 4-substituted benzoic acid or 1,4-*trans*-cyclohexanedicarboxylic acid using the carbodiimide method reported earlier[8] except for the ester *3b* which was synthesized using the acid chloride-Et_3N method.[8] All these esters were purified by column chromatography on silica gel using various mixtures of EtOAc or CH_2Cl_2 in hexane for the phenylbenzoates and CH_2Cl_2 for the cyclohexane diesters as the eluting solvents. The phenylbenzoates were recrystallized from hexane whereas the cyclohexane diesters were recrystallized from abs. EtOH. Purified yields ranged from 19.7–88.2%. Analytical data for typical examples are as follows:

3a (X = $C_{10}H_{21}$): IR (Nujol) 1720 (str, CO_2R) and 1710 (str, C═O) and 1620 cm^{-1} (wk, Ar) and NMR (FT) δ8.10 (d, J = 8.4 Hz, 2, ArH ortho to CO_2), 7.29 (d, J = 8.1 Hz, 2, ArH ortho to O), 7.21 (s, 2, ArH ortho to CH_2COC_8), 7.19 (s, 2, ArH ortho to $C_{10}H_{21}$), 3.68 (s, 2, $ArCH_2CO$), 2.69 (t, J = 7.4 Hz, 2, $ArCH_2$), 2.45 (t, J = 7.2 Hz, 2, $COCH_2C_7$) and 1.85–0.6 (m, 34, C_9H_{19} and C_7H_{15}); *3a* (X = $C_{10}H_{21}O$): IR (Nujol) 1740 (str CO_2R), 1720 (str C═O) and 1610 cm^{-1} (wk, Ar) and NMR (FT) δ8.05 (d, J = 9.0 Hz, 2, ArH ortho to CO_2), 7.10 (s, 4, ArH ortho to CH_2 and O_2CAr), 6.90 (d, J = 9.0 Hz, 2, ArH ortho to OR), 4.00 (t, J = 7.0 Hz, 2,CH_2OAr), 3.65 (s, 2, $ArCH_2CO$), 2.42 (t, J = 7.0 Hz, 2, $COCH_2C_7$) and 2.20–0.60 (m, 34, C_9H_{19} and C_7H_{15}); *3b* (X = $C_{10}H_{21}$): IR (Nujol) 1720 (str, CO_2R), 1700 (str C═O) and 1615 cm^{-1} (med, Ar) and NMR δ8.00 (d, J = 8.0

Hz, 2, ArH ortho to CO_2), 7.18 (d, J = 8.0 Hz, 2, ArH ortho to O), 7.08 (s, 2, ArH ortho to CH_2CH_2COR), 7.04 (s, 2, ArH ortho to C_{10}), 3.00–2.50 (m, 6, $ArCH_2$ and $CH_2CH_2COC_7$), 2.32 (t, J = 7.0 Hz, 2, $COCH_2C_6$), 2.00–0.66 (m, 32, C_9H_{19} + C_6H_{13}) and *3b* (X = $C_{10}H_{21}O$): IR (Nujol) 1735 (str CO_2R), 1735 (str C=O) and 1590 cm^{-1} (wk, Ar) and NMR δ8.12 (d, J = 6.8 Hz, 2, ArH ortho to CO_2), 7.21 (d, J = 7.48 Hz, 2, ArH ortho to CH_2), 7.10 (d, J = 9.0 Hz, 2, ArH ortho to O_2C), 6.97 (d, J = 8.9 Hz, 2, ArH ortho to O), 4.02 (t, J = 6.7 Hz, 2, $ArOCH_2$), 2.90 (t, J = 7.3 Hz, 2, $Ar\underline{CH_2}CH_2CO$), 2.72 (t, J = 7.4 Hz, 2, $ArCH_2\underline{CH_2}CO$), 2.38 (t, J = 7.4 Hz, 2, $CO\underline{CH_2}C_6$), 1.81 (t, J = 6.8 Hz, 2, $ArOCH_2\underline{CH_2}$), 1.66–0.88 (m, 24, $12CH_2$) and 0.88 (s, 6, 2Me).

Additional evidence that the esters *12* were formed in the Grignard reaction was obtained from the mass spectrum for the ester *2* (X = $C_{10}H_{21}O$, n = 2, R′ = C_7H_{15}) prepared from one of these phenols which showed major peaks at 526 (13.7%) for the calculated molecular weight, 525 (42.57%, M-1), 261 (100%, ), 154 (86.20%) and 145 (61.11%).

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