Synthesis of 3-Substituted Pentane-2,4-diones: Valuable Intermediates for Liquid Crystals

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Received November 16, 1994®

General procedures for the synthesis of six series of 3-substituted pentane-2,4-diones are described. The diones were used as intermediates in the preparation of pyrazoles, isoxazoles, and coordination complexes whose mesogenic properties have been studied. Nematic and smectic phases have been obtained in a number of cases, and the relationship between molecular structure and mesogenic properties has been explored.

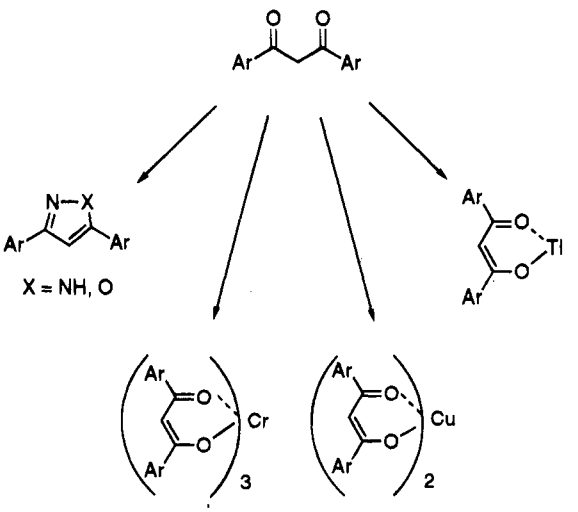
Introduction

The field of liquid crystals has incorporated numerous different organic systems in both low and high molecular weight materials.[1,2] In recent years, the synthesis of metal-containing mesogenic compounds has opened a new area of research with many future possibilities.[3] However, despite the large number of liquid crystalline compounds described to date, it is possible to find new molecular structures that could be suitable for new technological applications.[4]

In the course of our research program involving the synthesis of novel liquid crystals, we wished to use different β-diketone derivatives as synthetic intermediates. 1,3-Disubstituted propane-1,3-diones are classic examples of precursors for the synthesis of mesogenic heterocycles or metallomesogenic derivatives. Mesogenic pyrazoles and isoxazoles obtained *via* β-diketones have been described previously in the literature,[5] and β-diketones have been widely used as organic ligands in mesogenic coordination complexes of some transition metals such as Cu(II),[6] Tl(I),[7] Cr(III),[8] V(IV),[9] and Pd(II)[10] (Chart 1).

In contrast, only a few examples of mesogenic 3-substituted pentane-2,4-diones have been published.[11] These compounds could be valuable intermediates in the synthesis of calamitic derivatives, both with or without

Chart 1



metals. The β-diketone group incorporates a strong dipole moment which is still present in the heterocyclic derivatives or, in many cases, in the metal complex derivatives. This polar group could help to increase the anisotropy of the molecular polarizability and consequently favor mesogenic behavior.[12] This paper deals with the synthesis and characterization of six new series of 3-substituted pentane-2,4-diones (Chart 2) and their pyrazole, isoxazole, and Cu(II) complex derivatives (Chart 3). A different synthetic strategy has been proposed for each series of β-diketones, and a discussion of the synthetic methods has been undertaken. In order to study the influence of the molecular core on mesogenic properties, two different terminal groups have been introduced: R as a linear decyl group (series **a**) or a 4-(*n*-decyloxy)benzoyl group (series **b**) (see Chart 2). The mesogenic behavior of the compounds has been studied, and a comparative study of the properties observed in the different derivatives has been included.

Results and Discussion

A. Synthesis. Synthesis of 3-Decylpentane-2,4-dione (1). The most general procedure for the synthesis of 3-alkylpentane-2,4-diones is the C-alkylation of the pentane-2,4-dione (acetylacetone) under various conditions. Although different methodologies for alkylation

® Abstract published in *Advance ACS Abstracts,* April 15, 1995.

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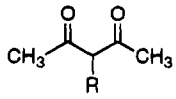
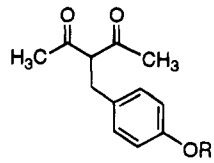
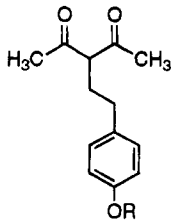
Chart 2



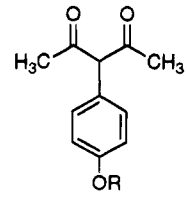
1 R = -$C_{10}H_{21}$



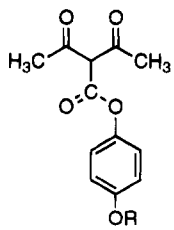
2 R = H
2a R = -$C_{10}H_{21}$
2b R = -CO-C_6H_4-O$C_{10}H_{21}$



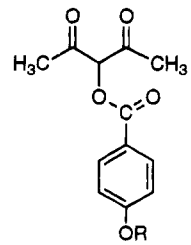
3 R = H
3a R = -$C_{10}H_{21}$
3b R = -CO-C_6H_4-O$C_{10}H_{21}$



4 R = H
4a R = -$C_{10}H_{21}$
4b R = -CO-C_6H_4-O$C_{10}H_{21}$

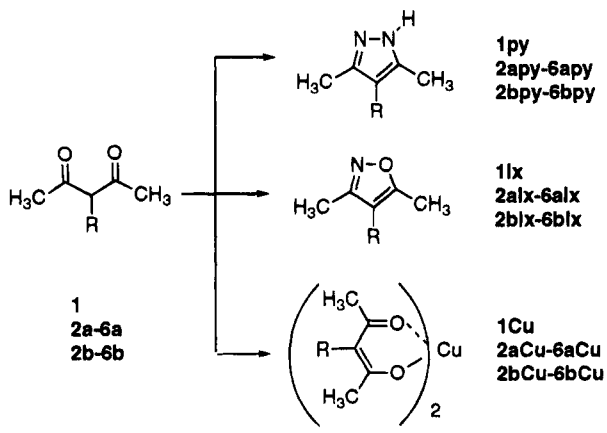


5 R = H
5a R = -$C_{10}H_{21}$
5b R = -CO-C_6H_4-O$C_{10}H_{21}$



6 R = H
6a R = -$C_{10}H_{21}$
6b R = -CO-C_6H_4-O$C_{10}H_{21}$

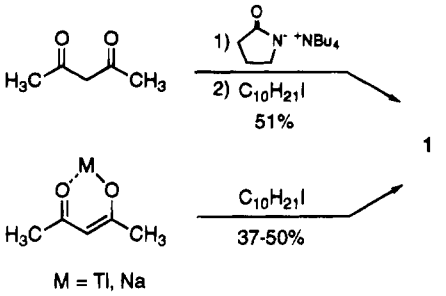
Chart 3



have been published, which have proved useful in most cases, the use of an alkylating agent with a long chain creates problems such that, in our experience, most of the classical procedures were not useful in the preparation of the target compounds described here. Indeed, the most typical conditions involving the use of acetylacetone with decyl bromide as the alkylating agent in the presence of potassium carbonate gave, under all conditions tested, only moderate yields of the corresponding O-alkylation products as a mixture of *Z* and *E* stereoisomers even after very long reaction times.

Although the use of 1-alkenes as alkylating agents with acetylacetone in the presence of metal oxides, such as lead(IV) oxide, has been reported,[13] all attempts using 1-decene and acetylacetone in the presence of the catalyst under general conditions were unsuccessful and the starting products were quantitatively recovered.

Scheme 1



Phase transfer catalysis[14] (PTC) has proven to be an efficient procedure for the selective C-alkylation of β-diketones, and numerous papers have been published describing the use of a wide variety of ammonium salts.[15-18] To the best of our knowledge, however, there are no specific procedures dealing with the problem of using an alkyl halide with a long chain as an alkylating agent. All our attempts using most of the commercially available ammonium salts failed, except in the case of tetrabutylammonium 2-pyrrolidonate,[18] which gave selective C-alkylation of acetylacetone when decyl iodide was used as the alkylating agent and dimethylformamide as the solvent.

Many successful efforts have been made using metal enolates of β-diketones to achieve selective C-alkylation, and a wide variety of metals (Zn,[19] Cu,[20] Ni,[21] Tl,[22] Na,[23] and Co[24]) and conditions have been described. Unfortunately, however, our attempts to use this approach with decyl iodide met with failure. For example, although the use of cobalt(II) acetyl acetonate has been reported as one of the best methods for achieving selective C-alkylation of β-diketones using alkyl halides, when decyl halides were used under all conditions which we tried, the starting products were recovered. Only thallium and sodium enolates gave moderate yields of the C-alkylation product when decyl iodide was used as the alkylating agent (Scheme 1).

Synthesis of 3-[(4-Hydroxyphenyl)methyl]pentane-2,4-dione (2). The use of sodium or thallium enolates usually prevents the formation of O-alkylation products, and this methodology is especially useful in the

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(15) (a) D'Incan, E.; Viout P. *Tetrahedron* **1978**, *34*, 2469. (b) D'Incan, E.; Viout, P. *Tetrahedron* **1975**, *31*, 159.
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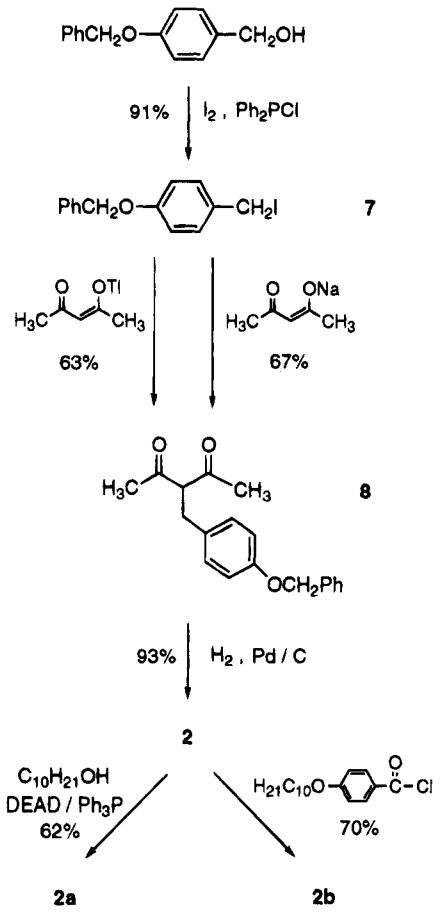
Scheme 2

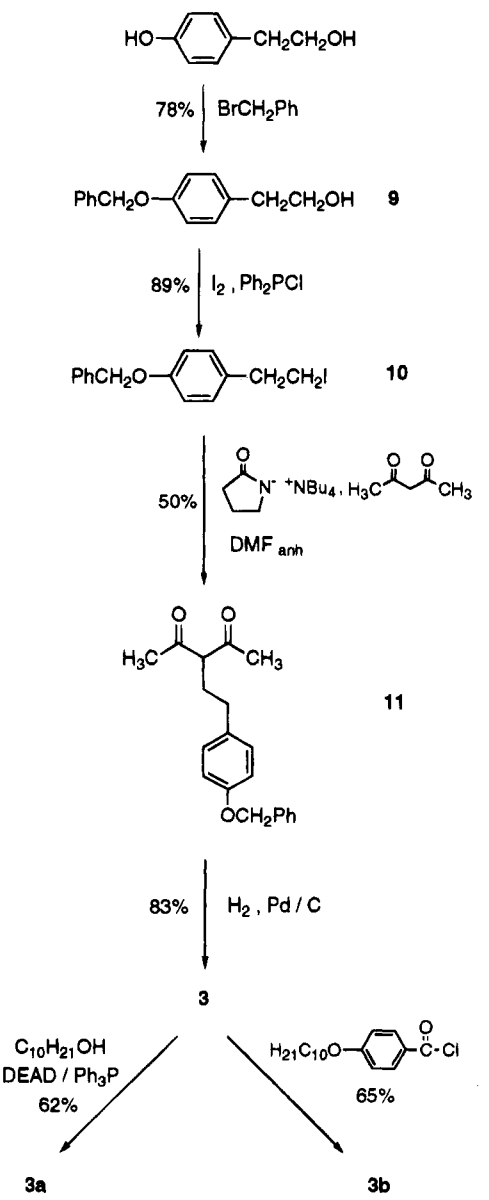


case of the most reactive benzyl halides. In our case, these enolates allowed for the synthesis of the desired products, minimizing the amount of di-C-alkylation products obtained by carefully controlling the reaction conditions. These reactions are outlined in Scheme 2.

The use of sodium or thallium enolates involves the use of the corresponding benzyl iodide, in which the phenolic hydroxy group is suitably protected so that the desired groups can be incorporated at the end of the synthetic route. The starting material, 4-(benzyloxy)-benzyl iodide (**7**), was easily prepared from the commercially available 4-(benzyloxy)benzyl alcohol using chlorodiphenylphosphine and iodine.[25] After the selective C-alkylation of the sodium or thallium enolates, the resulting product was deprotected through a typical hydrogenolysis reaction using hydrogen and Pd/C to give **2**, which was subsequently alkylated to give **2a** using 1-decanol, diethyl azodicarboxylate (DEAD), and Ph_3P[26] or benzoylated to give **2b** using 4-(*n*-decyloxy)benzoyl chloride.

Synthesis of 3-[2-(4-Hydroxyphenyl)ethyl]pentane-2,4-dione (3). In the synthesis of this compound, each enolate we tried gave decomposition products and again only with sodium or thallium enolates did reaction occur, although low yields (up to 10%) were obtained even in the most favorable conditions while using 2-[4-(benzyloxy)phenyl]ethyl iodide (**10**). After many attempts, only with the methodology of phase transfer catalysis (PTC) and while using tetrabutylammonium 2-pyrrolidonate could moderate yields of the desired product be obtained.

Scheme 3



The complete strategy involves the use of the alkyl iodide **10**, which can be easily obtained from the corresponding alcohol **9** using chlorodiphenylphosphine and iodine.[25] Williamson etherification of the commercially available 2-(4-hydroxyphenyl)ethanol allows for the synthesis of **9**. After the selective C-alkylation of acetylacetone, easy deprotection of the hydroxy group is possible through a hydrogenolysis reaction using hydrogen and Pd/C. **3** can be easily O-alkylated with the desired alcohol, 1-decanol in this case, in the presence of DEAD/Ph_3P to give **3a** and acylated with 4-(*n*-decyloxy)benzoyl chloride to give **3b** (Scheme 3).

Synthesis of 3-(4-Hydroxyphenyl)pentane-2,4-dione (4). It has been reported[27] that sodium enolates of β-dicarbonyl compounds can be selectively arylated with aryl iodides in the presence of CuI, and we attempted the synthesis of compound **4** using this method. It proved to be a general and useful procedure in the synthesis of the desired products. The complete synthetic route is given in the Scheme 4.

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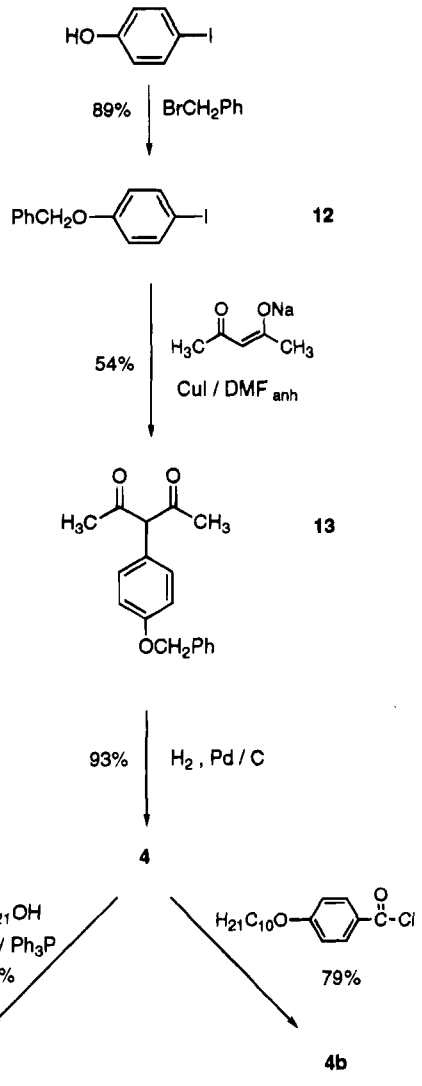
Scheme 4

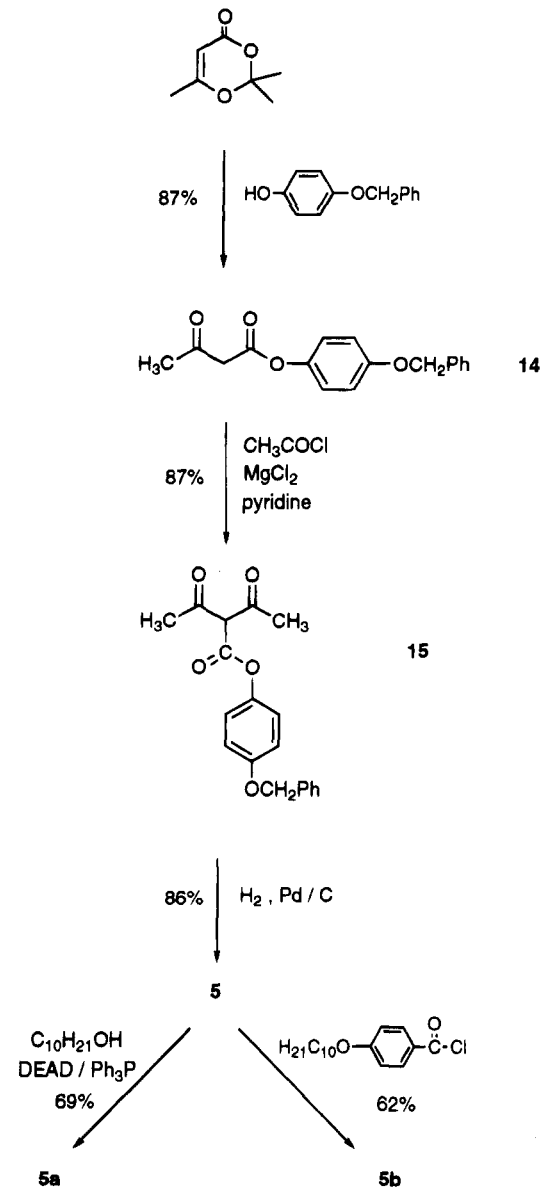


The Williamson reaction is useful for preparing **12** from the commercially available 4-iodophenol. After arylation of the acetylacetone, the hydroxy group was deprotected using hydrogen and Pd/C to give **4**, which can easily be O-alkylated with the appropriate alcohol in the presence of DEAD/Ph_3P to give **4a** or acylated with 4-(*n*-decyloxy)-benzoyl chloride to give **4b**.

Synthesis of 4-Hydroxyphenyl 2-Acetyl-3-oxobutanoate (5). The use of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (dioxinone) as an intermediate in the synthesis of β-keto esters when reacted with nucleophiles has been reported,[28] and this method seemed to be the most appropiate for the preparation of the target compound (**5**), using 4-(benzyloxy)phenol as the nucleophile. Dioxinone was reacted with 4-(benzyloxy)phenol to give compound **14** in excellent yield, which was then reacted with acetyl chloride in the presence of $MgCl_2$/Py,[29] deprotected with hydrogen Pd/C, and finally, O-alkylated with the corresponding alcohol in the presence of DEAD/Ph_3P to give the desired product **5a** or acylated with 4-(*n*-decyloxy)benzoyl chloride to give **5b**. (Scheme 5)

Synthesis of 2,4-Dioxo-3-pentyl 4-Hydroxybenzoate (6). The phase transfer catalyst method is probably the most appropriate for the synthesis of compounds with the general structure **6** (Chart 2). The synthesis

Scheme 5



was undertaken using the available 3-chloropentane-2,4-dione (**17**) and the corresponding carboxylate in the presence of quaternary ammonium salts as catalysts. In this case, 4-(benzyloxy)benzoic acid (**16**), obtained from 4-hydroxybenzoic acid using the Williamson reaction, and 3-chloropentane-2,4-dione, obtained from acetylacetone and sulfuryl chloride, were reacted using tetrabutylammonium hydrogen sulfate as the catalyst to give **18** in good yield. This compound was easily deprotected and O-alkylated or O-acylated using the methods described previously (Scheme 6).

Synthesis of Pyrazoles, Isoxazoles, and Copper Complexes. The most general procedure for the synthesis of pyrazoles and isoxazoles is the reaction of 1,3-dicarbonyl compounds with hydrazine or hydroxylamine,[30] respectively.

Pyrazoles were easily prepared from β-diketones and hydrazine hydrate in ethanol or acetic acid,[31] and isoxazoles were prepared by condensation–cyclization of 1,3-

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(29) Rathke, M. W.; Cowan, P. J. *J. Org. Chem.* **1985**, *50*, 2622.
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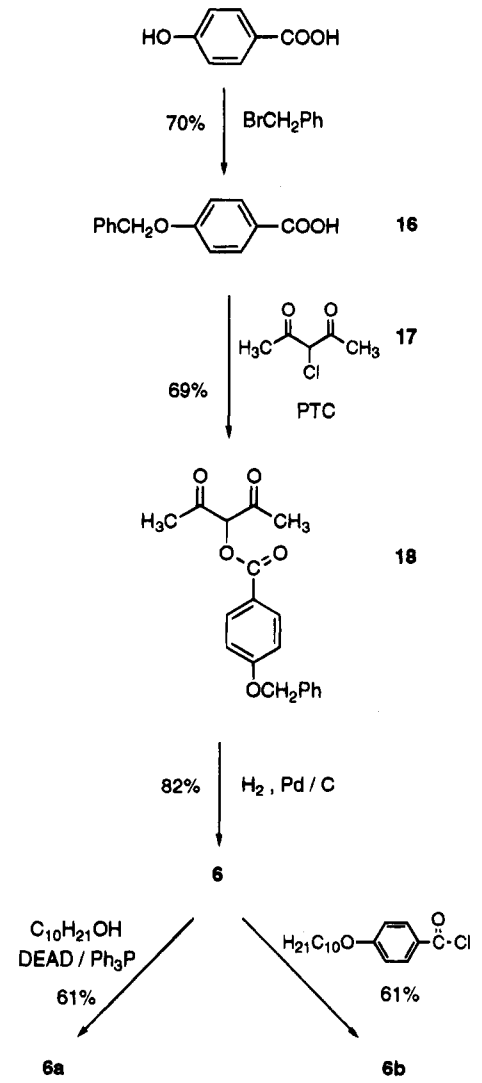
(31) (a) Rither, R. *Helv. Chim. Acta* **1952**, *35*, 478. (b) Nye, M. J.; Tang, W. P. *Tetrahedron* **1972**, *28*, 455.

Scheme 6



diketones with hydroxylamine hydrochloride in ethanol or acetic acid. In some cases, the intermediate 5-hydroxyisoxazoline can be isolated and converted into the isoxazole by treatment with hydrochloric acid.

Under appropriate conditions, β-diketones react with metal cations to form complexes in which the metal replaces the enolic hydrogen and a six-membered chelate ring is produced.

A wide variety of methods have been reported for the preparation of copper complexes. In the work described here, the complexes were easily obtained by the reaction of the β-diketone and copper(II) acetate.

B. Mesogenic Characterization. The optical, thermal, and thermodynamic data of the β-diketones and their derivatives are given in Tables 1 and 2.

All mesophases have been identified according to their textures observed by optical microscopy.[32] The β-diketones **5b** and **6b** both exhibit two monotropic phases[33] (N and S_A). Once the isotropic liquid is cooled, a schlieren texture allows us to identify a nematic phase. Once it is cooled further, focal–conic texture appears in the S_A phase and this last texture is easily transformed into a homeotropic texture by the application of mechanical stress.

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Table 1. Optical, Thermal, and Thermodynamic Data for the β-Diketones 1, 2a–6a, and Their Derivatives

compound	transition	temp (°C)	ΔH (kJ/mol)
1	C_1–C_2	−13.0	15.7
	C_2–I	0.3	8.9
1py	C_1–C_2	25.3	23.5
	C_2–I	39.7	2.1
1Ix	C–I	−2.4	22.5
1Cu	C–I	145.2	94.5
2a	C–I	31.8	39.1
2apy	C–I	95.7	22.7
2aIx	C–I	28.8	38.2
2aCu	C–I	136.8	87.0
3a	C–I	−21.8	16.7
3apy	C–I	76.9	27.8
3aIx	C_1–C_2	−45.8	8.3
	C_2–C_3	−31.6	−21.0[a]
	C_3–I	25.2	29.1
3aCu	C_1–C_2	84.0	6.8
	C_2–C_3	102.1	1.2
	C_3–C_4	110.6	1.9
	C_4–C_5	124.1	3.1
	C_5–C_6	136.0	9.7
	C_6–I	149.9	42.3
4a	C_1–C_2	−8.4	−13.0[a]
	C_2–I	9.8	14.0
4apy	C–I	100.7	36.6
4aIx	C_1–C_2	8.3	27.0
	C_2–I	23.0	30.4
4aCu	C_1–I	93.9	88.4
	C_2–I	96.3	
5a	C_1–C_2	44.8	33.4
	C_2–I	54.1	6.1
5apy	C_1–C_2	24.8	−1.1[a]
	C_2–C_3	74.5	16.0
	C_3–C_4	80.4	−7.3[a]
	C_4–I	88.5	19.7
5aIx	C_1–C_2	−50.6	2.1
	C_2–C_3	−28.7	−12.4[a]
	C_3–C_4	−9.2	−11.9[a]
	C_4–I	53.4	40.5
5aCu	C_1–C_2	109.4	68.8
	C_2–I	148.9	25.7
6a	C_1–C_2	−54.9	1.7
	C_2–C_3	−18.4	−3.3[a]
	C_3–C_4	−7.5	1.8
	C_4–C_5	−3.3	−5.6[a]
	C_5–I	6.6	8.0
6apy	C_1–I	86.6	27.7
	C_2–I	90.7	
6aIx	C_1–C_2	−27.9	−15.3[a]
	C_2–C_3	−15.0	17.1
	C_3–C_4	8.7	−10.5[a]
	C_4–I	19.9	10.8
6aCu	C_1–C_2	82.9	11.3
	C_2–I[b]	207.5	46.8

[a] Crystal–crystal* exothermic transitions. [b] Partial decomposition.

Pyrazole derivatives **5bpy** and **6bpy** show a schlieren texture typical of a nematic phase (Figure 1). Finally, the copper complex **6bCu** shows, in the heating process, a marbled texture, but unfortunately, this is accompanied by thermal decomposition which makes the study of the phase on cooling impossible.

C. Mesogenic Behavior. A characteristic observed in the compounds described in this paper is that most of them exhibit crystalline polymorphism. This phenomenon is very common in mesogenic and promesogenic compounds. However, only a small number of compounds show mesomorphism. Figure 2 shows two representative examples of this behavior in the isoxazole **3aIx** and a copper complex **5bCu**.

(33) When the thermotropic mesophase appears both in the heating and cooling process, it is called enantiotropic. The thermodynamically unstable mesophases, which only appear in the cooling process due to the hysteresis in the crystallization point, are referred to as monotropic.

Table 2. Optical, Thermal, and Thermodynamic Data for the β-Diketones 2b–6b and Their Derivatives

compound	transition	temp (°C)	ΔH (kJ/mol)
2b	C_1–I	49.8	42.7
	C_2–I	55.8	
2bpy	C_1–C_2	49.7	0.6
	C_2–C_3	75.8	2.2
	C_3–C_4	101.3	1.1
	C_4–I	136.7	25.0
2bIx	C–I	57.6	36.5
2bCu	C_1–C_2	151.8	25.5
	C_2–I[a]	205.6	66.9
3b	C_1–C_2	4.9	9.2
	C_2–C_3	36.3	3.6
	C_3–I	50.4	9.9
3bpy	C_1–C_2	123.2	3.2
	C_2–I	140.7	27.1
3bIx	C–I	57.0	37.6
3bCu	C_1–C_2	94.2	16.3
	C_2–C_3	127.3	6.1
	C_3–C_4	135.4	5.0
	C_4–I[a]	184.3	50.1
4b	C–I	94.5	37.5
4bpy	C–I	149.7	32.2
4bIx	C_1–C_2	8.5	−25.6[b]
	C_2–C_3	36.8	2.4
	C_3–I	70.4	30.4
4bCu	C_1–C_2	154.6	4.2
	C_2–I[a]	209.6	39.2
5b	C_1–C_2	27.7	3.8
	C_2–I	65.9	37.5
	I–N[c]	50.7	−0.4
	N–S_A[c]	45.2	−0.4
5bpy	C_1–C_2	68.6	2.3
	C_2–C_3	94.3	4.4
	C_3–I	156.0	31.6
	I–N[c]	145.9[d]	
5bIx	C_1–C_2	63.2	14.4
	C_2–I	82.0	28.7
5bCu	C_1–C_2	77.8	3.3
	C_2–C_3	93.7	35.5
	C_3–C_4	116.4	11.7
	C_4–I[a]	210.3	21.8
6b	C_1–C_2	25.1	1.0
	C_2–C_3	46.4	18.3
	C_3–I	79.4	15.6
	I–N[c]	27.5	−0.9
	N–S_A[c]	24.9	−0.6
6bpy	C–I	125.3	21.4
	I–N[c]	78.9	−0.9
6bIx	C–I	101.9	33.2
6bCu	C_1–C_2	186.4	24.6
	C_2–N[a]	221.8	46.4
	N–I	225.9	5.4

[a] Partial decomposition. [b] Crystal–crystal* exothermic transitions. [c] Monotropic transition. [d] Date of optical microscopy.

Series a. In spite of the low melting points, none of the compounds of series **a** (short promesogenic units) exhibit mesogenic behavior. Most of the β-diketone and isoxazole derivatives of series **a** are liquid at room temperature, whereas the pyrazole and copper complex derivatives have higher melting points. In both cases, the increase in intermolecular forces is responsible for the increase in the melting temperatures: hydrogen bonds in pyrazoles[5a] and metal–oxygen interactions in copper complexes.[34]

In general, in compounds of series **a**, the length-to-breadth ratio is clearly low and does not favor the parallel molecular organization typical of the liquid crystal state. Even in the case of the copper derivatives, which have a dimeric structure, this length is insufficient to promote mesophase formation. An additional factor in the case of the copper complexes is their higher melting points in comparison with the homologous organic derivatives, which may prevent the appearance of mesomorphism.

(34) Alonso, P. J.; Marcos, M.; Martinez, J. I.; Orera, V. M.; Sanjuan, M. J.; Serrano, J. L. *Liq. Cryst.* **1993**, *13*, 585.

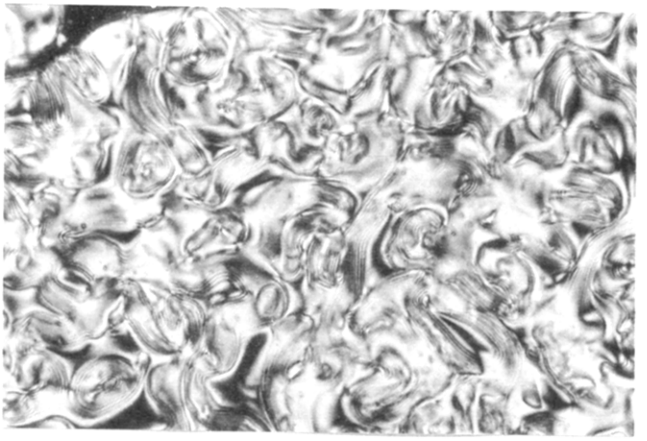

Figure 1. Schlieren texture of the nematic phase observed in pyrazole **5bpy** (crossed polarizers, 145 °C).

Series b. Most of the compounds in series **b** have higher transition temperatures than the corresponding compounds in series **a**. However, both types of compounds (**a** and **b**) maintain the same relative behavior, and in addition, the pyrazole and copper complex derivatives in series **b** have higher transition temperatures than the β-diketone and isoxazole derivatives.

As can be seen in Table 2, only the derivatives in which the core unit is attached to the β-diketone moiety *via* a carboxyl group are mesogenic (**5b**, **5bpy**, **6b**, **6bpy**, and **6bCu**).

The **6bCu** derivative exhibits an enantiotropic nematic phase, whereas in the other compounds, only monotropic phases are observed.

D. Structure–Mesomorphism Relationship. The mesogenic behavior observed can be explained using geometrical and electronic factors associated with the molecular structure. The length-to-breadth ratio is greater in compounds of series **b** than those in series **a**, and consequently, mesomorphism is favored. However, liquid crystal phases only appear when the group joining the mesogenic core to the β-diketone group allows for extended conjugation between the two groups.

The linking groups CH_2 and CH_2CH_2 disrupt the electronic conjugation, and, even when the phenyl group is directly joined to β-diketone, conjugation is prevented due to steric factors (see Figure 3).

In these three series of compounds, the phenyl 4-(*n*-decyloxy)benzoate group acts as a classic promesogenic unit and we can consider the β-diketone as a voluminous terminal group which strongly impedes the parallel molecular arrangement necessary for mesophase formation.

In contrast, when the linking group is an ester, the aromatic conjugation can be extented to the β-diketone, and this fact favors molecular planarity and also increases the anisotropy of the electronic polarizability, thus increasing molecular interactions (van der Waals forces) and consequently promoting liquid crystal behavior.

It is interesting to note that the isoxazole derivatives do not exhibit mesogenic behavior. The isoxazole structure is isoelectronic to the pyrazole and β-diketone homologues. However, the last two groups have a proton which increases the intermolecular interactions by means of intermolecular H bonds. The presence of H bonds is

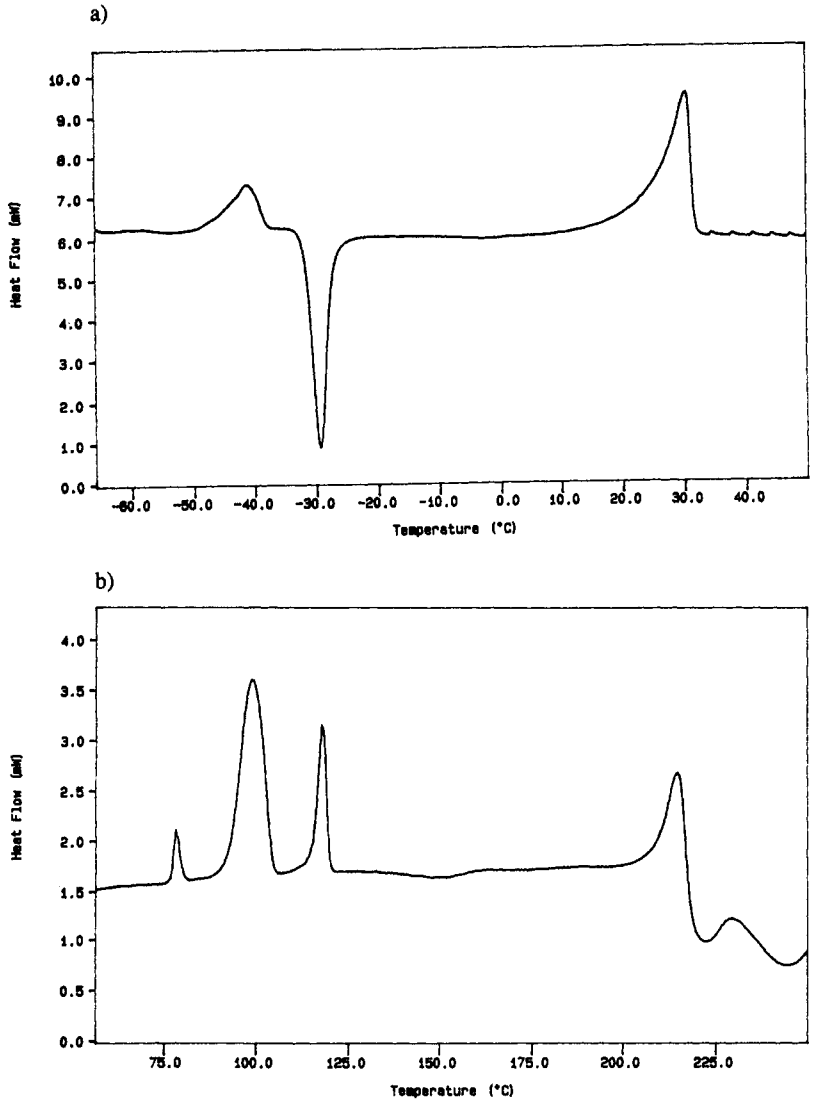

Figure 2. Crystalline polymorphism. (a) Heating DSC traces for the isoxazole **3aIx**. (b) Heating DSC traces for the copper complex **5bCu**.

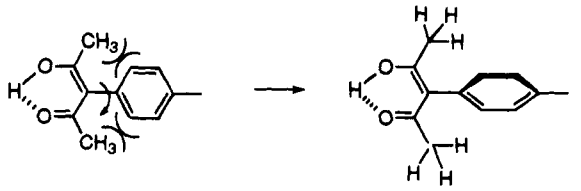

Figure 3.

a fundamental factor in the mesomorphism observed in these compounds.

Conclusion

Six new series of 3-substituted pentane-2,4-diones have been synthesized and studied as valuable intermediates to liquid crystals. In each case, after a complete study, a different strategy has been chosen in order to obtain the best results and yields. These synthetic methods allow for the synthesis of a wide variety of β-diketones, opening the way to new liquid crystalline materials or compounds with nonlinear optical properties. The mesogenic properties of the β-diketones and their corresponding pyrazole, isoxazole, and copper(II) complex derivatives have been studied. In general, the β-diketone group significantly increases the molecular width and makes the parallel alignment of the molecules necessary for the appearance of mesomorphism difficult. Consequently, mesogenic behavior is only observed in β-diketones, pyrazoles, and copper complexes in which the promesogenic unit 4-[[4-(*n*-decyloxy)benzoyl]oxy]phenyl is attached to the β-diketone moiety through a carboxyl group. This group allows for extended conjugation through the molecule and emphasizes the importance of electronic factors in mesophase formation.

Experimental Section

General Considerations. Melting points were determined using a capillary melting point apparatus and are uncorrected. Chemical shifts (δ) are given in parts per million and the coupling constants (J) in hertz. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer. The optical textures of the mesophases were studied with a Nikon polarizing microscope equipped with a Mettler FP82 hot stage and a FP80 central processor and with an Olympus (BH-2) polarizing microscope equipped with a Linkam THMS 600 hot stage. The transition temperatures were measured by differential scanning calorimetry using either a Perkin-Elmer DSC-2 or DSC-7 instrument operated at a scanning rate of 10 °C min^{-1} on heating. The calorimeters were calibrated with *n*-octane (−56.8 °C, 176.4 J/g), indium (156.6 °C, 28.4 J/g), and tin (232.1 °C, 60.46 J/g) as standards. TLC was performed on Merck precoated silica gel plates which were visualized using UV

light. Flash column chromatography was performed using 230–400 mesh silica gel (Merck). Organic solutions were dried over anhydrous magnesium sulfate. The yields given below are for purified products.

In this section, only general procedures have been described. Spectral data for all compounds have been included as supplementary material.

Synthesis of 3-*n*-Decylpentane-2,4-dione (1). Procedure I. A mixture of 1-decyl iodide (4.02 g, 15 mmol) and sodium acetyl acetonate[23] (1.46 g, 12 mmol) in methyl ethyl ketone (30 mL) was heated under reflux for 72 h. The solvent was distilled off, and water (20 mL) was added to the residue, which was extracted with ether (4 × 25 mL) and dried. After evaporation of the solvent, the crude product was purified on a silica gel column, using dichloromethane as eluent, to give 1.47 g of **1** (51% yield).

Procedure II. A mixture of thallium(I) acetyl acetonate[22a] (3.64 g, 12 mmol) and 1-decyl iodide (4.02 g, 15 mmol) in 25 mL of 1,4-dioxane was heated under reflux (N_2 atmosphere) for 48 h. The mixture was then cooled to room temperature and filtered. After evaporation of the solvent, the crude product was purified on a silica gel column, using dichloromethane as eluent, to give 1.06 g of **1** (37% yield).

Procedure III. To a solution of acetylacetone (670 mg, 6.7 mmol) in dry DMF (5 mL) was added a solution of tetrabutylammonium 2-pyrrolidonate (10 mmol) in dry DMF, obtained by the reaction of tetrabutylammonium fluoride, 2-pyrrolidone, and *tert*-butyldimethylsilyl chloride.[18] The reaction mixture was stirred for 15 min at room temperature. 1-Decyl iodide (3.37 g, 10 mmol) was added, and the solution was stirred for 72 h at room temperature. The mixture was then poured into an aqueous solution of ammoniun chloride (25 mL), extracted with ether (4 × 30 mL), and dried. After evaporation of the solvent, the crude product was purified on a silica gel column, using dichloromethane as eluent, to give 0.8 g of **1** (50% yield).

Synthesis of 4-(Benzyloxy)benzyl Iodide (7). A solution of iodine (4.06 g, 16 mmol) in toluene (50 mL) was added dropwise at room temperature to a stirred solution of 4-(benzyloxy)benzyl alcohol (2.57 g, 12 mmol), chlorodiphenylphosphine (3.5 g, 16 mmol), and imidazole (1.85 g, 27 mmol) in toluene (150 mL). After 15 min, the reaction was complete. The mixture was poured into an equal volume of saturated aqueous sodium carbonate, and the organic phase was washed with aqueous sodium thiosulfate solution, washed with water, and dried. The solvent was then evaporated, and the residue was chromatographed on a silica gel column, using dichloromethane as eluent, to give 3.54 g of **7** (91% yield), mp 87.3 °C. Anal. Calcd for $C_{14}H_{13}OI$: C, 51.85; H, 4.04. Found: C, 51.79; H, 4.10.

Synthesis of 3-[[4-(Benzyloxy)phenyl]methyl]pentane-2,4-dione (8). Procedure I. A mixture of 4-(benzyloxy)-benzyl iodide (3.24 g, 10 mmol) and sodium acetyl acetonate (1.22 g, 10 mmol) in methyl ethyl ketone (20 mL) was heated under reflux for 1 h. The solvent was distilled off, and water (15 mL) was added to the residue, which was extracted with ether (3 × 15 mL) and dried. After evaporation of the solvent, the crude product was purified on a silica gel column, using a mixture of hexane:ethyl acetate (3:1) as eluent, to afford 1.98 g of **8** (67% yield).

Procedure II. A mixture of thallium(I) acetyl acetonate (1.515 g, 5 mmol) and 4-(benzyloxy)benzyl iodide (1.62 g, 5 mmol) in dry acetone (40 mL) was stirred under nitrogen for 5 h at 0 °C. The mixture was then filtered. After evaporation of the solvent, the crude product was purified on a silica gel column, using a mixture of hexane:ethyl acetate (3:1) as eluent, to give 1.86 g of **8** (63% yield), mp 44.4 °C. Anal. Calcd for $C_{19}H_{20}O_3$: C, 76.99; H, 6.81. Found: C, 77.10; H, 6.79.

Synthesis of 2-[4-(Benzyloxy)phenyl]ethanol (9). A solution of 2-(4-hydroxyphenyl)ethanol (3.45 g, 25 mmol), benzyl bromide (4.7 g, 27.5 mmol), and anhydrous potassium carbonate (3.8 g, 27.5 mmol) in dry acetone (50 mL) was heated under reflux for 2 days. The solution was then filtered, the solvent removed, and the residue dissolved in ether (50 mL). The ethereal solution was washed with 2% sodium hydroxide solution (3 × 15 mL) and dried. The solvent was evaporated, and the crude product was recrystallized from hexane to give 4.45 g of **9** (78% yield), mp 84.8 °C. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.91; H, 7.07. Found: C, 79.03; H, 6.96.

Synthesis of 2-[4-(Benzyloxy)phenyl]ethyl Iodide (10). A solution of iodine (4.06 g, 16 mmol) in toluene (50 mL) was added dropwise at room temperature to a stirred solution of 2-[4-(benzyloxy)phenyl]ethanol (2.74 g, 12 mmol), chlorodiphenylphosphine (3.5 g, 16 mmol), and imidazole (1.85 g, 27 mmol) in toluene (150 mL). After 15 min, the reaction was complete. The reaction mixture was poured into an equal volume of saturated aqueous sodium carbonate solution. The organic phase was washed with aqueous sodium thiosulfate, washed with water, and dried. The solvent was evaporated, and the residue was chromatographed on a silica gel column, using dichloromethane as eluent, to give 4.06 g of **10** (89% yield), mp 77 °C. Anal. Calcd for $C_{15}H_{15}OI$: C, 53.25; H, 4.47. Found: C, 53.39; H, 4.60.

Synthesis of 3-[2-[4-(Benzyloxy)phenyl]ethyl]pentane-2,4-dione (11). To a solution of acetylacetone (670 mg, 6.7 mmol) in anhydrous dimethylformamide (5 mL) was added a solution of tetrabutylammonium 2-pyrrolidonate, (10 mmol) in anhydrous dimethylformamide, obtained by the reaction of tetrabutylammonium fluoride, 2-pyrrolidone, and *tert*-butyldimethylsilyl chloride.[18] The reaction mixture was stirred for 15 min at room temperature, and 2-[4-(benzyloxy)phenyl]-ethyl iodide (3.38 g, 10 mmol) was added. The mixture was stirred for 72 h at room temperature, poured into ammonium chloride solution (25 mL), extracted with ether (4 × 30 mL), and dried. After evaporation of the solvent, the crude product was purified on a silica gel column, using dichloromethane as eluent, to give 1.04 g of **11** (50% yield), mp 83 °C. Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.38; H, 7.15. Found: C, 77.19; H, 7.20.

Synthesis of 4-(Benzyloxy)iodobenzene (12). To a solution of iodophenol (2.2 g, 10 mmol) and potassium hydroxide (0.56 g, 10 mmol) in ethanol (10 mL) was added benzyl bromide (1.88 g, 11 mmol), and the mixture was heated under reflux for 24 h. The solvent was removed, and the residue was dissolved in ether (15 mL), washed with 2% sodium hydroxide aqueous solution (3 × 10 mL), and dried. The solvent was evaporated, and the crude product was chromatographed on a silica gel column, using hexane:ether (9:1) as eluent, to give 2.76 g of **12** (89% yield), mp 61.2 °C. Anal. Calcd for $C_{13}H_{11}OI$: C, 50.32; H, 3.58. Found: C, 50.46; H, 3.61.

Synthesis of 3-[4-(Benzyloxy)phenyl]pentane-2,4-dione (13). 4-(Benzyloxy)iodobenzene (2.48 g, 8 mmol) was dissolved in anhydrous dimethylformamide (10 mL). Copper-(I) iodide (1.52 g, 8 mmol) and sodium acetyl acetonate (4.88 g, 40 mmol) were added successively to the reaction mixture under a nitrogen current. The reaction mixture was heated for 12 h at 100°C. The mixture was cooled to room temperature, poured into an equal volume of water, extracted with ether, and dried. After evaporation of the solvent, the crude product was purified on a silica gel column, using a mixture hexane:ether (4:1) as eluent, to give 1.22 g of **13** (54% yield), mp 93 °C. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.56; H, 6.43. Found: C, 76.47; H, 6.52.

Synthesis of 4-(Benzyloxy)phenyl 3-Oxobutanoate (14). A solution of 4-(benzyloxy)phenol (2 g, 10 mmol) and 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (1.42 g, 10 mmol) in xylene (4 mL) was placed in a 50 mL flask. The flask was immersed in an oil bath preheated to 150 °C and the solution was vigorously stirred. The evolution of acetone became apparent within several minutes; heating was continued for a total of 40 min, and the xylene was removed. The crude product was purified on a silica gel column, using dichloromethane as eluent, to give 2.47 g of **14** (87% yield), mp 89.2 °C. Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.80; H, 5.68. Found: C, 71.83; H, 5.71.

Synthesis of 4-(Benzyloxy)phenyl 2-Acetyl-3-oxobutanoate (15). To a stirred mixture of dry magnesium chloride (0.48 g, 5 mmol) and dry dichloromethane (10 mL), under argon, was added 4-(benzyloxy)phenyl 3-oxobutanoate (1.42 g, 5 mmol). The mixture was cooled to 0 °C, pyridine (0.79 g, 10 mmol) was added, and the mixture was stirred for 15 min. Acetyl chloride (0.39 g, 5 mmol) was added, and the mixture was stirred at 0 °C for 15 min and a further 6 h at room temperature. The mixture was again cooled to 0 °C, the reaction was quenched with 6 M hydrochloric acid (3 mL), and the mixture was extracted with ether (3 × 10 mL) and dried.

The ether was removed, and the residue was recrystallized from hexane to give 1.42 g of **15** (87% yield), mp 97 °C. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.91; H, 5.56. Found: C, 70.01; H, 5.39.

Synthesis of 4-(Benzyloxy)benzoic Acid (16). A mixture of 4-hydroxybenzoic acid (6.9 g, 50 mmol), potassium hydroxide (6.16 g, 0.11 mol), and benzyl bromide (9.42 g, 55 mmol) in ethanol:water (160 mL/16 mL) was heated under reflux for 20 h. Aqueous potassium hydroxide solution (20%, 60 mL) was added, and the mixture was heated under reflux for a further 4 h. The reaction mixture was allowed to cool, water was added, and the solution was acidified with 2 M hydrochloric acid. The precipitate was filtered off and recrystallized from ethanol to give 7.98 g of **16** (70% yield), mp 190.3 °C. Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.66; H, 5.30. Found: C, 73.74; H, 5.28.

Synthesis of 3-Chloropentane-2,4-dione (17). A solution of sulfuryl chloride (5.4 g, 40 mmol) dissolved in anhydrous toluene (10 mL) was added dropwise to a solution of acetylacetone (4 g, 40 mmol) in anhydrous toluene (40 mL). The mixture was stirred for 48 h at room temperature, and water (40 mL) was added. The mixture was stirred overnight, the organic phase dried, and the solvent removed. The crude product was purified by vacuum distillation to give 2.8 g of **17** (52% yield).

Synthesis of 2,4-Dioxo-3-pentyl 4-(Benzyloxy)benzoate (18). 4-(Benzyloxy)benzoic acid (2.28 g, 10 mmol) and tetrabutylammonium hydrogen sulfate (3.4 g, 10 mmol) were dissolved in 5 mL of 2 M sodium hydroxide solution, and the mixture was stirred for 30 min. The solution was extracted with dichloromethane (3 × 15 mL) and dried. 3-Chloropentane-2,4-dione (2 g, 15 mmol) was added, and the solution was heated under reflux for 24 h. The organic material was washed with 2.5 M sulfuric acid (2 × 10 mL) and water (3 × 10 mL) and dried. The residue obtained after evaporation of the solvent was purified on a silica gel column, using dichloromethane as eluent, to give 2.25 g of **18** (69% yield), mp 79.3 °C. Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.91; H, 5.56. Found: C, 69.78; H, 5.48.

Hydrogenolysis: General Procedure for Compounds 2, 3, 4, 5, and 6. A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with a mixture of benzyl ether (**8**, **11**, **13**, **15**, or **18**, respectively) (10 mmol) and 2 g of 10% palladium/carbon in dichloromethane (20 mL) was hydrogenated at room temperature and atmospheric pressure. After 8 h, the reaction was complete. The mixture was filtered and the solvent evaporated. The crude product was purified on a silica gel column.

3-[(4-Hydroxyphenyl)methyl]pentane-2,4-dione (2): eluent hexane:ethyl acetate (1:1); yield 93%; mp 94.8 °C. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.87; H, 6.85. Found: C, 69.99; H, 6.97.

3-[2-(4-Hydroxyphenyl)ethyl]pentane-2,4-dione (3): eluent hexane:ethyl acetate (3:1); yield 83%; mp 123 °C. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.87; H, 7.33. Found: C, 70.71; H, 7.49.

3-(4-Hydroxyphenyl)pentane-2,4-dione (4): eluent hexane:ether (3:2); yield 93%; mp 95.7 °C. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.72; H, 6.30. Found: C, 68.86; H, 6.24.

4-Hydroxyphenyl 2-acetyl-3-oxobutanoate (5): eluent: dichloromethane:ether (9:1); yield 86%; mp 122.6 °C. Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.00; H, 5.12. Found: C, 61.11; H, 5.23.

2,4-Dioxo-3-pentyl 4-hydroxybenzoate (6): eluent hexane:ether (1:4); yield 82%; mp 119.8 °C. Anal. Calcd for $C_{12}H_{12}O_5$: C, 61.00; H, 5.12. Found: C, 61.09; H, 5.18.

Etherification: General Procedure for compounds 2a, 3a, 4a, 5a, and 6a. A solution of diethyl azodicarboxylate (1.74 g, 10 mmol) was added dropwise to a solution of triphenylphosphine (3.144 g, 12 mmol), β-diketone (**2**, **3**, **4**, **5**, or **6**, respectively) (10 mmol), and 1-decanol (1.58 g, 10 mmol) in ether (10 mL) at room temperature. A white precipitate of triphenylphosphine oxide and diethyl hydrazinedicarboxylate quickly appeared. After the mixture was stirred overnight at room temperature, the precipitate was removed by filtration. The solvent was evaporated *in vacuo* and the crude product purified on a silica gel column.

3-[[4-(*n*-Decyloxy)phenyl]methyl]pentane-2,4-dione (2a): eluent dichloromethane; yield 62%. Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.25; H, 9.90. Found: C, 76.40; H, 10.09.

3-[2-[4-(*n*-Decyloxy)phenyl]ethyl]pentane-2,4-dione (3a): eluent hexane:ethyl acetate (4:1); yield 62%.

3-[4-(*n*-Decyloxy)phenyl]pentane-2,4-dione (4a): eluent hexane:ether (12:1); yield 79%.

4-(*n*-Decyloxy)phenyl 2-acetyl-3-oxobutanoate (5a): eluent hexane:dichloromethane (3:7); yield 69%. Anal. Calcd for $C_{22}H_{32}O_5$: C, 70.17; H, 8.57. Found: C, 70.23; H, 8.49.

2,4-Dioxo-3-pentyl 4-(*n*-decyloxy)benzoate (6a): eluent hexane:ether (7:3); yield 61%.

Esterification: General Procedure for Compounds 2b, 3b, 4b, 5b, and 6b. A solution of 4-(*n*-decyloxy)benzoyl chloride (2.135 g, 7.2 mmol) in dichloromethane (5 mL) was added dropwise at 0 °C to a solution of β-diketone (**2**, **3**, **4**, **5**, or **6**, respectively) (6 mmol), 4-(dimethylamino)pyridine (117 mg, 0.96 mmol), and triethylamine (727 mg, 7.2 mmol) in dry dichloromethane (10 mL). The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent, the crude product was purified on a silica gel column.

4-(2-Acetyl-3-oxobutyl)phenyl 4-(*n*-decyloxy)benzoate (2b): eluent hexane:acetone (4:1); yield 70%. Anal. Calcd for $C_{29}H_{38}O_5$: C, 74.63; H, 8.21. Found: C, 74.71; H, 8.39.

4-(3-Acetyl-4-oxopentyl)phenyl 4-(*n*-decyloxy)benzoate (3b): eluent hexane:ethyl acetate (3:1); yield 65%. Anal. Calcd for $C_{30}H_{40}O_5$: C, 74.96; H, 8.39. Found: C, 75.13; H, 8.53.

4-(2,4-Dioxo-3-pentyl)phenyl 4-(*n*-decyloxy)benzoate (4b): eluent hexane:ether (4:1); yield: 79%. Anal. Calcd for $C_{28}H_{36}O_5$: C, 74.29; H, 8.02. Found: C, 74.36; H, 7.87.

4-[[4-(*n*-Decyloxy)benzoyl]oxy]phenyl 2-acetyl-3-oxobutanoate (5b): eluent dichloromethane; yield: 62%. Anal. Calcd for $C_{29}H_{36}O_7$: C, 70.13; H, 7.31. Found: C, 70.28; H, 7.09.

2,4-Dioxo-3-pentyl 4-[[4-(*n*-decyloxy)benzoyl]oxy]benzoate (6b): eluent hexane:ether (1:1); yield 61%. Anal. Calcd for $C_{29}H_{36}O_7$: C, 70.13; H, 7.31. Found: C, 70.04; H, 7.54.

Pyrazoles. General Procedure for Compounds 1py, 2apy, 3apy, 4apy, 2bpy, 3bpy, and 4bpy. A mixture of β-diketone (**1**, **2a**, **3a**, **4a**, **2b**, **3b**, or **4b**, respectively) (2 mmol) and hydrazine hydrate (120 mg, 2.4 mmol) was heated under reflux in ethanol (20 mL) for 2 h. The reaction mixture was poured into a saturated aqueous sodium chloride (20 mL) solution, extracted with dichloromethane (3 × 15 mL), and washed with water (3 × 15 mL). After evaporation of the solvent, the crude product was purified on a silica gel column.

4-*n*-Decyl-3,5-dimethylpyrazole (1py): eluent hexane:ethyl acetate (2:3); yield 86%. Anal. Calcd for $C_{15}H_{28}N_2$: C, 76.20; N, 11.86; H, 11.95. Found: C, 75.98; N, 11.82; H, 11.77.

4-[[4-(*n*-Decyloxy)phenyl]methyl]-3,5-dimethylpyrazole (2apy): eluent hexane:ethyl acetate (2:3); yield 59%. Anal. Calcd for $C_{22}H_{34}N_2O$: C, 77.30; N, 8.18; H, 10.01. Found: C, 77.38; N, 8.15; H, 9.87.

4-[2-[4-(*n*-Decyloxy)phenyl]ethyl]-3,5-dimethylpyrazole (3apy): eluent acetone:ether (1:9); yield 62%. Anal. Calcd for $C_{23}H_{36}N_2O$: C, 77.47; N, 7.86; H, 10.18. Found: C, 77.52; N, 7.90; H, 10.43.

4-[4-(*n*-Decyloxy)phenyl]-3,5-dimethylpyrazole (4apy): eluent: acetone:hexane (3:7); yield 89%. Anal. Calcd for $C_{21}H_{32}N_2O$: C, 76.77; N, 8.53; H, 9.82. Found: C, 76.71; N, 8.65; H, 10.11.

4-[(3,5-Dimethyl-4-pyrazolyl)methyl]phenyl 4-(*n*-decyloxy)benzoate (2bpy): eluent hexane:ethyl acetate (2:3); yield 61%. Anal. Calcd for $C_{29}H_{38}N_2O_3$: C, 75.28; N, 6.06; H, 8.28. Found: C, 75.31; N, 6.03; H, 8.39.

4-[2-(3,5-Dimethyl-4-pyrazolyl)ethyl]phenyl 4-(*n*-decyloxy)benzoate (3bpy): eluent methanol:ether (4:96); yield 71%. Anal. Calcd for $C_{30}H_{40}N_2O_3$: C, 75.58; N, 5.88; H, 8.46. Found: C, 75.45; N, 5.92; H, 8.67.

4-(3,5-Dimethyl-4-pyrazolyl)phenyl 4-(*n*-decyloxy)benzoate (4bpy): eluent acetone:hexane (2:3); yield 82%. Anal. Calcd for $C_{28}H_{36}N_2O_3$: C, 74.95; N, 6.26; H, 8.09. Found: C, 74.80; N, 6.30; H, 8.24.

Pyrazoles. General Procedure for Compounds 5apy, 6apy, 5bpy, and 6bpy. Hydrazine hydrate (120 mg, 2.4 mmol) was added to a solution of β-diketone (**5a**, **6a**, **5b**, or **6b**, repectively) (2 mmol) in acetic acid (20 mL). The reaction

mixture was stirred at room temperature for 3 h and poured into an equal volume of ice–water. The precipitate was filtrered off and washed with small portions of water.

4-(*n*-Decyloxy)phenyl 3,5-Dimethylpyrazole-4-carboxylate (5apy). The pyrazole was purified on a silica gel column, using hexane:ethyl acetate (3:7) as eluent (88% yield). Anal. Calcd for $C_{22}H_{32}N_2O_3$: C, 70.92; N, 7.52; H, 8.66. Found: C, 70.85; N, 7.55; H, 8.79.

3,5-Dimethyl-4-pyrazolyl 4-(*n*-Decyloxy)benzoate (6apy). The pyrazole was recrystallized from hexane (69% yield). Anal. Calcd for $C_{22}H_{32}N_2O_3$: C, 70.92; N, 7.52; H, 8.66. Found: C, 71.01; N, 7.56; H, 8.44.

4-[[4-(*n*-Decyloxy)benzoyl]oxy]phenyl 3,5-Dimethylpyrazole-4-carboxylate (5bpy). The pyrazole was purified on a silica gel column using hexane:ethyl acetate (2:3) as eluent (84% yield). Anal. Calcd for $C_{29}H_{36}N_2O_5$: C, 70.69; N, 5.69; H, 7.37. Found: C, 70.77; N, 5.73; H, 7.49.

3,5-Dimethyl-4-pyrazolyl 4-[[4-(*n*-decyloxy)benzoyl]-oxy]benzoate (6bpy). The pyrazole was recrystallized from hexane: yield 75%. Anal. Calcd for $C_{29}H_{36}N_2O_5$: C, 70.69; N, 5.69; H, 7.37. Found: C, 70.81; N, 5.64; H, 7.02.

Isoxazoles. General Procedure for Compounds 1Ix, 3aIx, and 3bIx. A mixture of β-diketone (**1**, **3a**, or **3b**, respectively) (2 mmol), hydroxylamine hydrochloride (166 mg, 2.4 mmol), and triethylamine (242 mg, 2.4 mmol) in ethanol (20 mL) was heated under reflux for 3 h. The reaction mixture was poured into water (20 mL) and extracted with dichloromethane (3 × 15 mL). After evaporation of the solvent, the crude product was purified on a silica gel column.

4-*n*-Decyl-3,5-dimethylisoxazole (1Ix): eluent hexane: ethyl acetate (6:1); yield 52%.

4-[2-[4-(*n*-Decyloxy)phenyl]ethyl]-3,5-dimethylisoxazole (3aIx): eluent hexane:ethyl acetate (4:1); yield 64%.

4-[2-(3,5-Dimethyl-4-isoxazolyl)ethyl]phenyl 4-(*n*-decyloxy)benzoate (3bIx): eluent hexane:ethyl acetate (4:1); yield 57%. Anal. Calcd for $C_{30}H_{39}NO_4$: C, 75.43; N, 2.93; H, 8.24. Found: C, 75.39; N, 2.88; H, 8.43.

Isoxazoles. General Procedure for Compounds 2aIx, 4aIx, 6aIx, 2bIx, 4bIx, and 6bIx. A mixture of β-diketone (**2a**, **4a**, **6a**, **2b**, **4b**, or **6b**, respectively) (2 mmol), hydroxylamine hydrochloride (166 mg, 2.4 mmol), and triethylamine (242 mg, 2.4 mmol), in ethanol (20 mL) was heated under reflux for 4 h. A few drops of dilute hydrochloric acid were added, and the mixture was heated under reflux for 1 h. The reaction mixture was poured into water (20 mL) and extracted with dichloromethane (3 × 15 mL). After evaporation of the solvent, the crude product was purified on a silica gel column.

4-[[(4-(*n*-Decyloxy)phenyl]methyl]-3,5-dimethylisoxazole (2aIx): eluent hexane:ethyl acetate (7:3); yield 57%. Anal. Calcd for $C_{22}H_{33}NO_2$: C, 76.91; N, 4.08; H, 9.69. Found: C, 77.21; N, 4.12; H, 10.03.

4-[4-(*n*-Decyloxy)phenyl]-3,5-dimethylisoxazole (4aIx): eluent hexane:ethyl acetate (95:5); yield 69%.

3,5-Dimethyl-4-isoxazolyl 4-(*n*-decyloxy)benzoate (6aIx). The mixture was heated under reflux for 10 h: eluent hexane: acetone (9:1); yield 78%.

4-[(3,5-Dimethyl-4-isoxazolyl)methyl]phenyl 4-(*n*-decyloxy)benzoate (2bIx): eluent hexane:ethyl acetate (7:3); yield 58%. Anal. Calcd for $C_{29}H_{37}NO_4$: C, 75.12; N, 3.02; H, 8.05. Found: C, 74.97; N, 3.06; H, 7.90.

4-(3,5-Dimethyl-4-isoxazolyl)phenyl 4-(*n*-decyloxy)-benzoate (4bIx): eluent hexane:ethyl acetate (9:1); yield 71%. Anal. Calcd for $C_{28}H_{35}NO_4$: C, 74.79; N, 3.12; H, 7.85. Found: C, 74.63; N, 3.09; H, 7.98.

3,5-Dimethyl-4-isoxazolyl 4-[[4-(*n*-Decyloxy)benzoyl]-oxy]benzoate (6bIx). The mixture was heated under reflux for 10 h: eluent hexane:acetone (8:2); yield: 71%. Anal. Calcd for $C_{29}H_{35}NO_6$: C, 70.55; N, 2.84; H, 7.15. Found: C, 70.67; N, 2.81; H, 6.91.

Isoxazoles. General Procedure for Compounds 5aIx and 5bIx. A mixture of β-diketone (**5a** or **5b**, respectively) (2 mmol), hydroxylamine hydrochloride (166 mg, 2.4 mmol), and triethylamine (242 mg, 2.4 mmol) in acetic acid (15 mL) was stirred at room temperature for 50 h. During this time, the same quantity of hydroxylamine hydrochloride and triethylamine was added again twice. The reaction mixture was poured into water (20 mL) and stirred overnight. The precipitate was filtered off and washed with small portions of water. The crude product was purified on a silica gel column.

4-(*n*-Decyloxy)phenyl 3,5-dimethylisoxazole-4-carboxylate (5aIx): eluent dichloromethane; yield 50%. Anal. Calcd for $C_{22}H_{31}NO_4$: C, 70.73; N, 3.75; H, 8.37. Found: C, 70.68; N, 3.77; H, 8.53.

4-[[4-(*n*-Decyloxy)benzoyl]oxy]phenyl] 3,5-dimethylisoxazole-4-carboxylate (5bIx): eluent hexane:ethyl acetate (9:1); yield 43%. Anal. Calcd for $C_{29}H_{35}NO_6$: C, 70.55; N, 2.84; H, 7.15. Found: C, 70.67; N, 2.80; H, 7.33.

Copper(II) Complexes. General Procedure for Compounds 1Cu, 2aCu, 3aCu, 4aCu, 5aCu, 6aCu, 2bCu, 3bCu, 4bCu, 5bCu, and 6bCu. An ethanolic solution of β-diketone (**1**, **2a**, **3a**, **4a**, **5a**, **6a**, **2b**, **3b**, **4b**, **5b**, or **6b**, respectively) (1 mmol) was mixed with copper(II) acetate (100 mg, 0.5 mmol) dissolved in ethanol. The mixed solution was stirred for 1 h. The precipitate was filtered off and recrystallized.

Bis(3-*n*-decylpentane-2,4-dionato)copper(II) (1Cu): recrystallized from hexane; yield 78%. Anal. Calcd for $C_{30}H_{54}O_4Cu$: C, 65.50; H, 10.05. Found: C, 65.71; H, 9.88.

Bis[3-[[4-(*n*-decyloxy)phenyl]methyl]pentane-2,4-dionato]copper(II) (2aCu): recrystallized from ethyl acetate; yield 57%. Anal. Calcd for $C_{44}H_{66}O_6Cu$: C, 70.08; H, 8.83. Found: C, 70.16; H, 9.11.

Bis[3-[2-[4-(*n*-decyloxy)phenyl]ethyl]pentane-2,4-dionato]copper(II) (3aCu): recrystallized from ethyl acetate; yield 41%. Anal. Calcd for $C_{46}H_{70}O_6Cu$: C, 70.64; H, 9.03. Found: C, 70.67; H, 9.20.

Bis[3-[4-(*n*-decyloxy)phenyl]pentane-2,4-dionato]copper(II) (4aCu): recrystallized from ethanol; yield 74%. Anal. Calcd for $C_{42}H_{62}O_6Cu$: C, 69.48; H, 8.61. Found: C, 69.52; H, 8.79.

Bis[3-[[4-(*n*-decyloxy)phenoxy]carbonyl]pentane-2,4-dionato]copper(II) (5aCu): recrystallized from acetone; yield 77%. Anal. Calcd for $C_{44}H_{62}O_{10}Cu$: C, 64.92; H, 7.68. Found: C, 65.06; H, 7.83.

Bis[3-[[4-(*n*-decyloxy)benzoyl]oxy]pentane-2,4-dionato]-copper(II) (6aCu): recrystallized from acetone; yield 67%. Anal. Calcd for $C_{44}H_{62}O_{10}Cu$: C, 64.92; H, 7.68. Found: C, 64.84; H, 7.75.

Bis[3-[[4-[[4-(*n*-decyloxy)benzoyl]oxy]phenyl]methyl]-pentane-2,4-dionato]copper(II) (2bCu): recrystallized from ethyl acetate; yield 58%. Anal. Calcd for $C_{58}H_{74}O_{10}Cu$: C, 70.06; H, 7.51. Found: C, 69.91; H, 7.77.

Bis[3-[2-[4-[4-(*n*-decyloxy)benzoyl]phenyl]ethyl]pentane-2,4-dionato]copper(II) (3bCu): recrystallized from ethyl acetate; yield 43%. Anal. Calcd for $C_{60}H_{78}O_{10}Cu$: C, 70.49; H, 7.70. Found: C, 70.32; H, 7.38.

Bis[3-[4-[[4-(*n*-decyloxy)benzoyl]oxy]phenyl]pentane-2,4-dionato]copper(II) (4bCu): recrystallized from acetone;yield 73%. Anal. Calcd for $C_{56}H_{70}O_{10}Cu$: C, 69.61; H, 7.31. Found: C, 69.69; H, 7.52.

Bis[3-[[4-[[4-(*n*-decyloxy)benzoyl]oxy]phenoxy]carbonyl]pentane-2,4-dionato]copper(II) (5bCu): recrystallized from ethyl acetate; yield 71%. Anal. Calcd for $C_{58}H_{70}O_{14}Cu$: C, 66.07; H, 6.70. Found: C, 66.23; H, 6.93.

Bis[3-[[4-[[4-(*n*-decyloxy)benzoyl]oxy]benzoyl]oxy]-pentane-2,4-dionato]copper(II) (6bCu): recrystallized from ethyl acetate; yield 65%. Anal. Calcd for $C_{58}H_{70}O_{14}Cu$: C, 66.07; H, 6.70. Found: C, 66.16; H, 6.89.

Acknowledgment. This work has been supported by CICYT (Spain) under contracts MAT91-0962-C02-01, MAT93-0104, and MAT94-0717-C02-01.

Supplementary Material Available: ^1H NMR spectra for compounds **1**, **3a**, **4a**, **6a**, **1Ix**, **3aIx**, **4aIx**, **6aIx,** and **17** and spectral data (^1H NMR and IR) for all compounds (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9419394