

## **CHAPTER V**

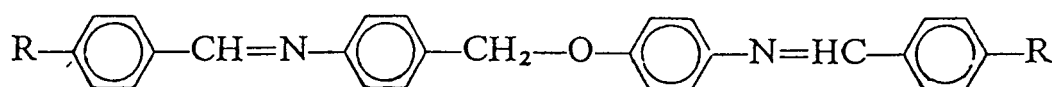
**Synthesis and thermal behaviour of  
[1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-alkyl-  
phenyl)propane]-1,3-diones, their copper(II)  
and oxovanadium(IV) complexes**

## 5.1 A brief account of the mesogenic properties of compounds containing methyleneoxy as a bridging group

Molecular linearity and rigidity are important requirements for a compound to exhibit a mesophase. A majority of calamitic mesogens contain phenyl rings linked by a number of different groups. Of these, groups such as  $-\text{CH}=\text{N}-$ ,<sup>1-3</sup>  $-\text{N}=\text{N}-$ ,<sup>4,5</sup>  $\text{N}=\text{N}$ ,<sup>1,4,6</sup>,  $-\text{C}=\text{C}-$ ,<sup>7-9</sup>  $\text{CH}=\text{N}$ ,<sup>10-12</sup>  $\text{C}\equiv\text{C}$ ,<sup>13-15</sup> and  $-\text{C}=\text{O}$ ,<sup>16-19</sup> have been used widely.

These linkage groups alter the linearity and polarisability of a given molecule to different extents. Compounds with bridging groups such as  $-\text{CH}_2-\text{CH}_2-$  and  $-\text{O}-\text{CH}_2-$  restrict the conjugation and also make a molecule less rigid. In a certain number of cases this flexibility renders the compound to give less thermally stable mesophases. As a matter of fact, these linkage groups have been purposefully used in some cases to bring down the melting as well as clearing temperatures.

The first mesogenic derivatives containing a methyleneoxy group, viz., 4,4'-bis[4-substitutedbenzylideneamino]-phenylbenzylethers (5.1) were reported several years ago by Rolle.<sup>24</sup> He found that the nematic phase in these compounds had a thermal range of about 66° to 80°C and very high clearing temperatures.

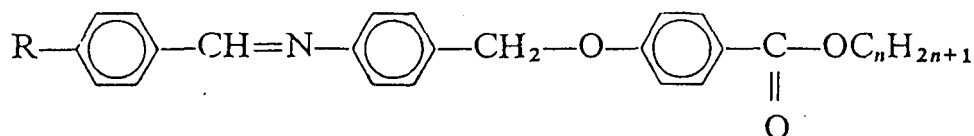


5.1

R = H, CH<sub>3</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub> or NO<sub>2</sub>

This was explained on the basis of the presence of two substituted benzylideneamine moieties in the molecule. When one of the substituted benzylideneamine unit was replaced by an ester group,<sup>25</sup> as shown in (5.2), the melting and clearing points were

decreased and the nematic thermal range also decreased ( $7-28^{\circ}\text{C}$ ) in the system.

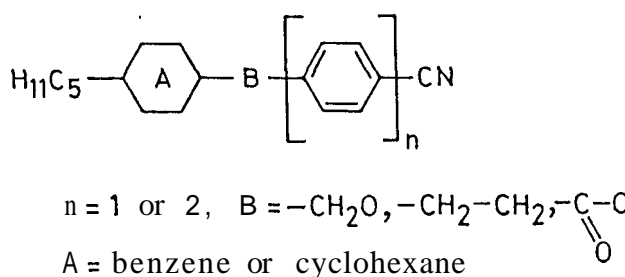


5.2

R = H, CH<sub>3</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub> or NO<sub>2</sub>

n = 1 or 2

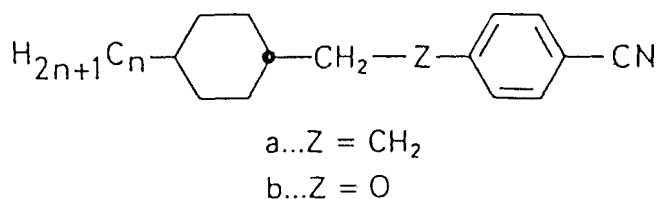
In the case of 4,4'-bis(4-nitrobenzyloxy)biphenyl,<sup>26</sup> the compound showed a monotropic nematic phase. In order to compare the effect of oxymethylene, dimethylene and ester bridging groups, in an aromatic system, Gray *et al.*<sup>20</sup> synthesised and studied the following compounds (5.3) and observed that the nematic-isotropic (N-I) temperature for oxymethylene linked compounds were lower than those for ester



5.3

linked compounds. However, the nematic-isotropic temperatures for dimethylene and oxymethylene compounds were similar and the melting points for dimethylene compounds were lowest among all these three linkage groups used in the compounds..

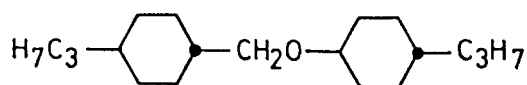
Carr *et al.*<sup>21</sup> also investigated the effect of oxymethylene linkage and dimethylene linkage groups on the mesomorphic properties in a system containing benzene and cyclohexane rings as shown in (5.4). They found that the N-I transition tempera-



5.4

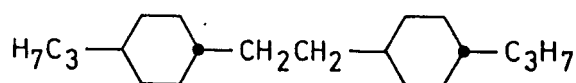
tures for both the linkages was almost the same. But the compound with oxymethylene bridging group showed comparatively a lower melting point. When the central linking group  $-\text{CH}_2-\text{O}-$  was reversed between phenyl and cyclohexyl rings and the oxygen atom was separated from conjugation with the aromatic ring, the mesophase thermal stability was further decreased.

A comparative study of oxymethylene, dimethylene and ester linkage groups in a completely saturated system was carried out by Osman.<sup>22</sup> He observed that dimethylene bridging group is most favourable for mesogenic property in such systems. Oxymethylene linkage lowers the efficiency of packing and gives lower clearing points. The ester linkage behaves similarly, but the delocalised  $\pi$  system leads to greater intermolecular attraction than the compound 5.5a resulting in a higher N-I temperature.



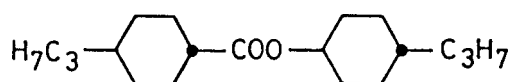
C 6.9 S 8.0 N 17.5 I

5.5a



C 34.6 S 73 I

5.5b



C 22.8 N 36.6 I

5.5c

In view of the above, it was felt that an oxymethylene linkage group between the two phenyl rings of a biphenyl moiety might also lower the melting point as also the thermal stability, of a mesophase. Also, there was no other report of a  $\beta$ -diketone system containing this group. Hence a number of such compounds and a few metal chelates of these have been synthesised and the results of the same have been discussed in this chapter.

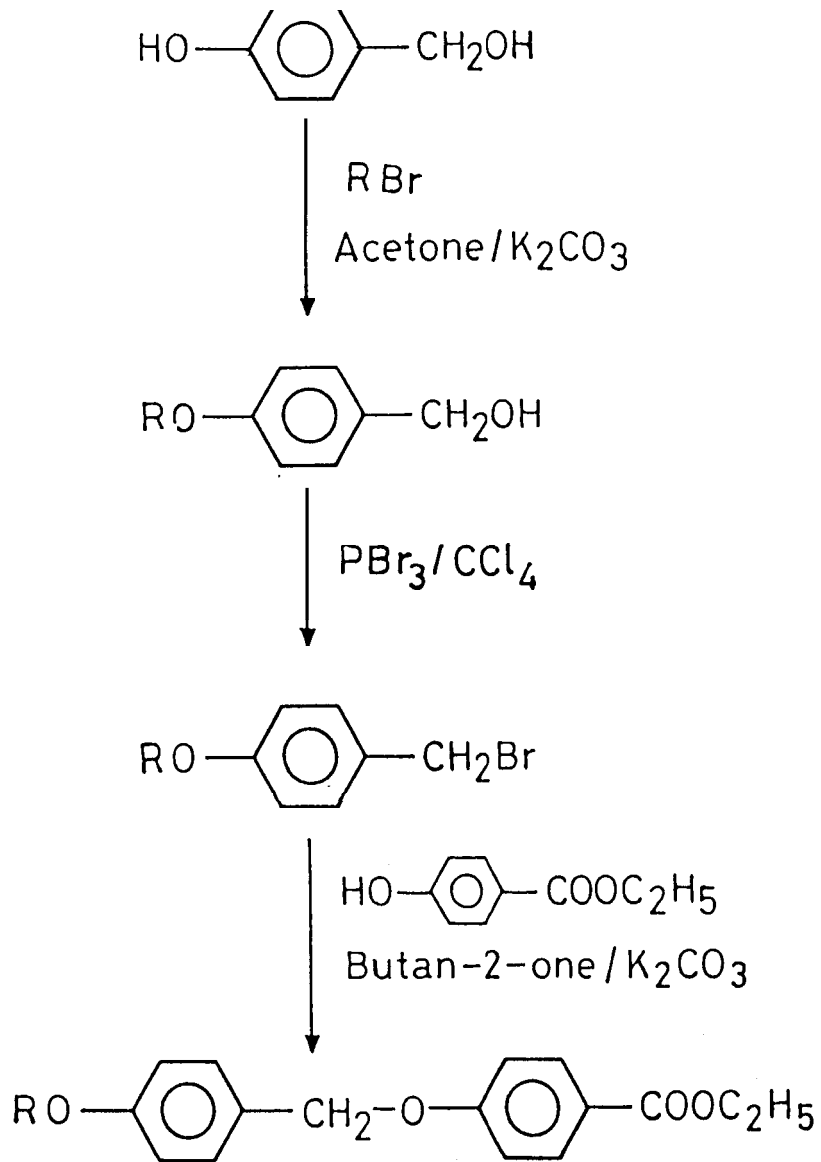
## 5.2 Synthesis

The synthesis of [1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-alkylphenyl)-propane]-1,3-diones, their copper(II) and oxovanadium(IV) complexes was carried out according to the schemes shown in figures 5.1, 5.2 and 5.3 respectively. O-Alkylation of 4-hydroxybenzyl alcohol using an appropriate n-alkylbromide in the presence of anhydrous potassium carbonate in dry acetone gave the corresponding 4-n-alkoxybenzyl alcohols. Bromination of 4-n-alkoxybenzyl alcohols using phosphorus tribromide yielded 4-n-alkoxybenzylbromides. These were condensed with ethyl-4-hydroxybenzoate in the presence of potassium carbonate to yield ethyl(4-n-alkoxybenzyloxy)benzoates.

n-Alkylphenylketones were prepared by acylating benzene with an appropriate acylhalide using Friedel-Crafts reaction to furnish n-alkylphenylketones. These on Wolff-Kishner reduction afforded n-alkylbenzenes which were again acylated using acetyl chloride to afford the desired 4-n-alkylacetophenones.

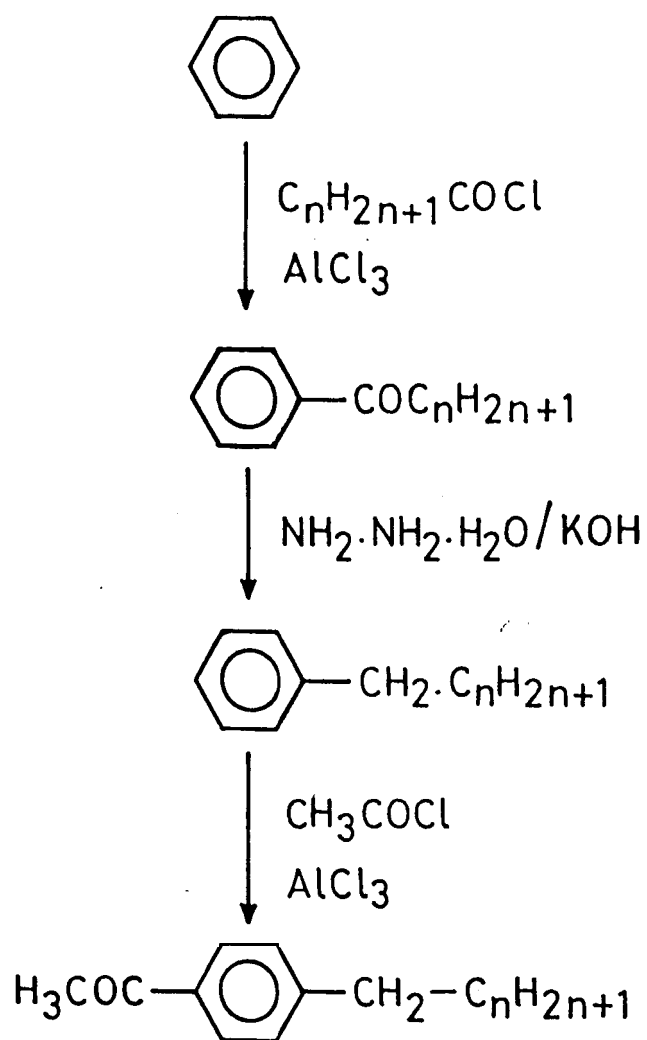
Claisen condensation of the above esters and methylketones yielded the respective  $\beta$ -diketones in fairly good yield. These  $\beta$ -diketones exist in the enolic form, which could be clearly seen in the PMR spectrum as shown in figure 5.4.

The copper(II) complexes were obtained by treating the potassium salt of an appropriate  $\beta$ -diketone in warm ethylalcohol with an ethanolic solution of cupric chloride dihydrate at room temperature. Similarly, the oxovanadium(IV) complexes of these ligands were synthesised in approximately 30% yield by slow addition of an alcoholic solution of vanadyl sulphate pentahydrate and aqueous sodium acetate to

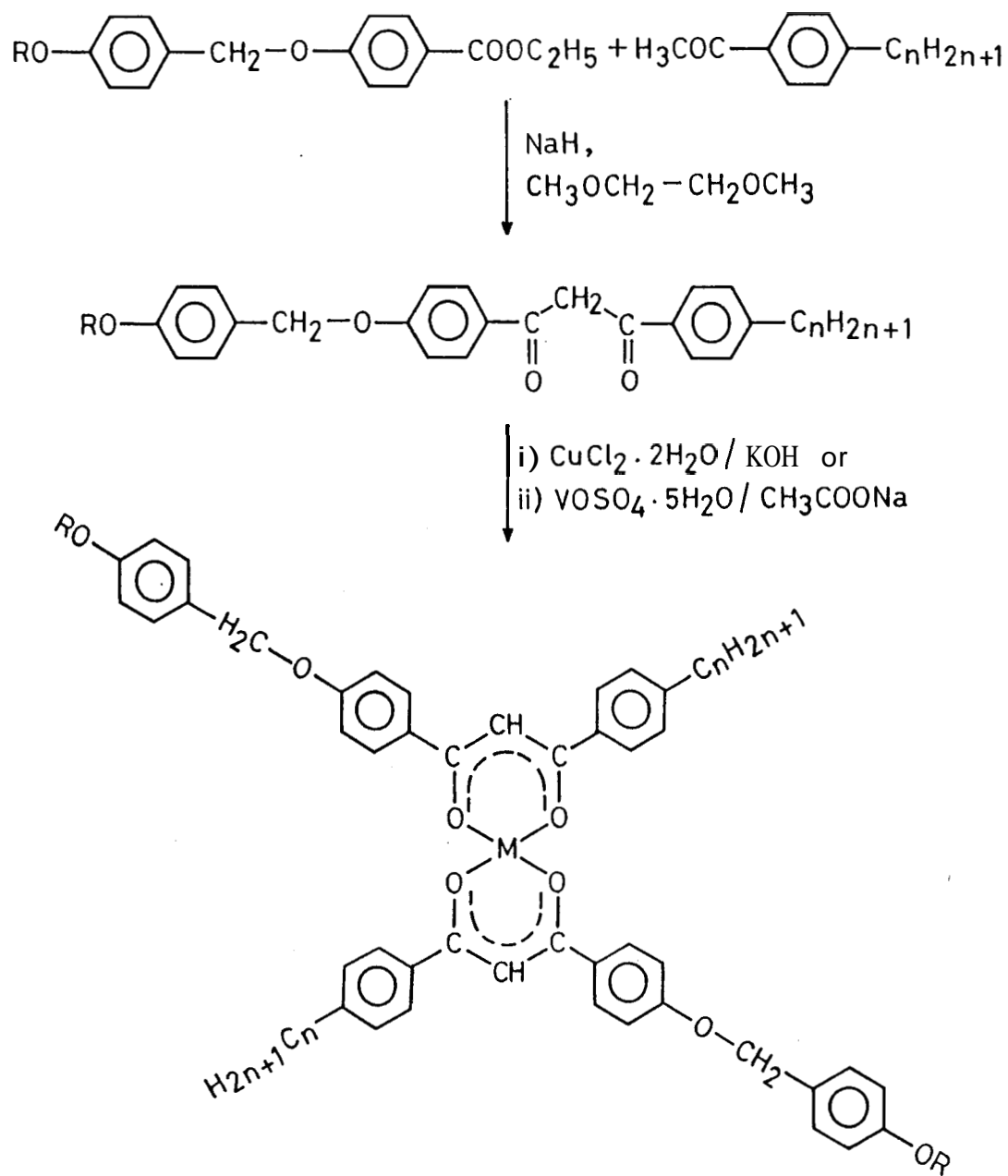


$\text{R} = \text{C}_2\text{H}_5, \text{C}_7\text{H}_{15}, \text{C}_{12}\text{H}_{25}$

**Figure 5.1**



**Figure 5.2**



$R = \text{C}_2\text{H}_5, \text{C}_7\text{H}_{15} \text{ or } \text{C}_{12}\text{H}_{25}$   
 $n = 1, 4, 6 \text{ or } 12$   
 $M = \text{Cu} \text{ or } \text{VO}$

**Figure 5.3**



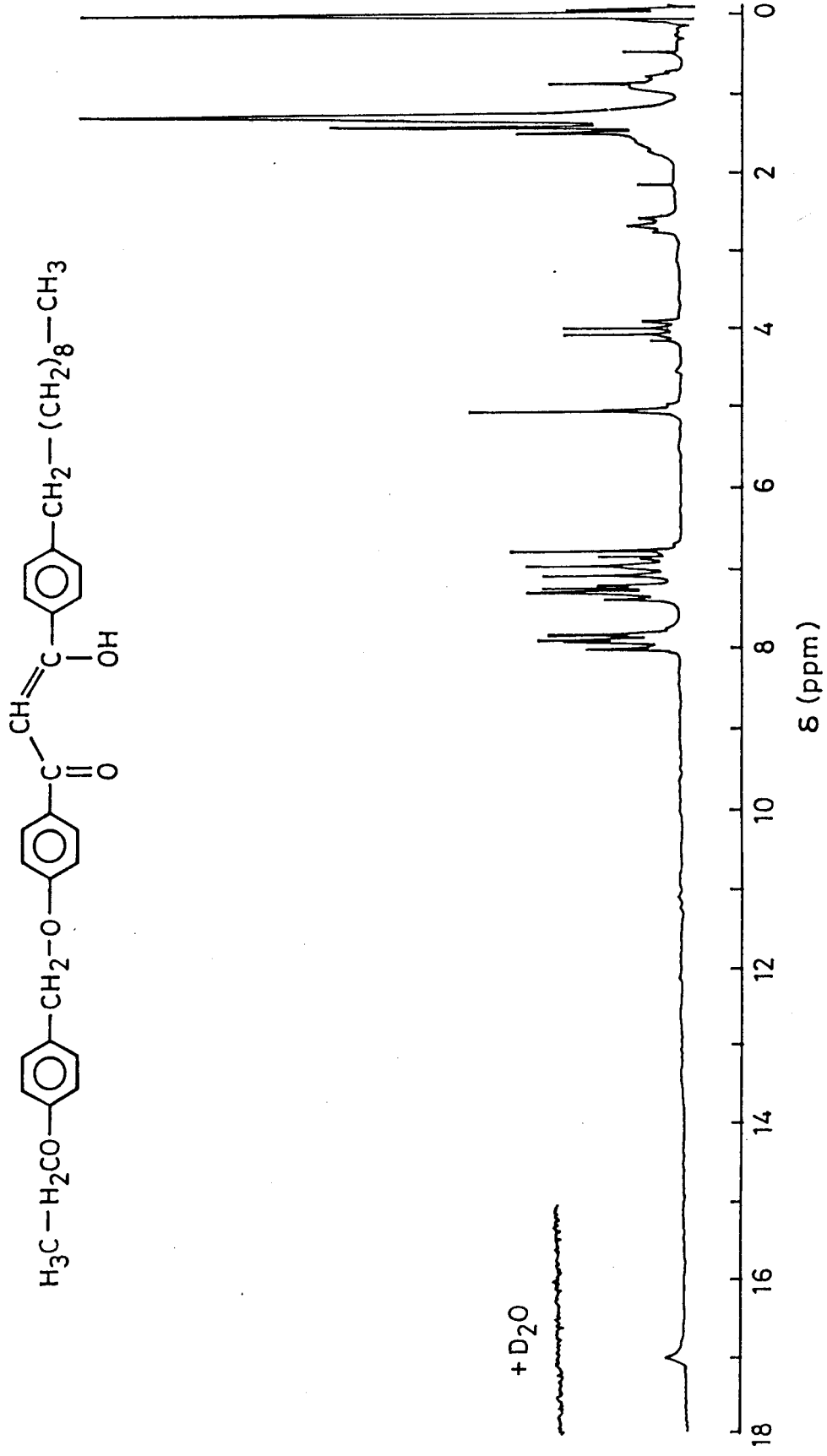


Fig.5.4. 80 MHz PMR spectrum of the compound 5.a.9 in CDCl<sub>3</sub> containing 1% TMS.

a warm alcoholic solution of the  $\beta$ -diketones. Repeated crystallisation from ethyl alcohol-chloroform mixture gave pure complexes. The position of V=O stretching band in the infrared spectrum is very diagnostic for the presence of linear chain structure and this band undergoes a shift to lower energy ( $<900\text{ cm}^{-1}$ ) with linear chain formation.<sup>28,29</sup> These complexes exhibit V=O stretching band around  $985\text{-}990\text{ cm}^{-1}$ . Figure 5.5 shows an infrared spectrum of compound 5.c.1.

### 5.3 Results and discussion

As mentioned earlier, the methyleneoxy bridging group was used in an attempt to lower the transition temperatures of some  $\beta$ -diketones and their metal chelates. The compounds investigated include [1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-alkylphenyl)propane-1,3-diones and bis[1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-alkylphenyl)propane-1,3-dionato]copper(II) and few of their oxovanadium(IV) congeners. In this  $\beta$ -diketone system, presence of the methyleneoxy group between two phenyl rings lowers the melting and clearing points as compared to the compounds, without the bridging group ( $\beta$ -diketones containing a biphenyl moiety). The melting points of the metal chelates have also decreased considerably as expected, but no mesophase was observed in these complexes.

The transition temperatures and the associated heats of transitions of the synthesised ligands are summarised in table 5.1. An examination of this table indicates that most of the compounds exhibit smectic C ( $S_C$ ) and smectic A ( $S_A$ ) phases. The first four compounds in this table belong to a series of [1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-alkylphenyl)propane]-1,3-diones. The lowest member of this series is non-mesogenic, while the middle member ( $n=4$ , 5.a.2), exhibits an enantiotropic  $S_A$  phase. The hexyl derivative ( $n=6$ , 5.a.3) exhibits a monotropic  $S_C$  phase in addition to the enantiotropic  $S_A$  phase. In the dodecyl derivative ( $n=12$ , 5.a.4) both the phases are enantiotropic in nature. On cooling the isotropic liquid this compound shows a simple focal-conic texture and at a lower temperature this changes to a broken focal-conic texture and these have been characterised as  $S_A$  and  $S_C$  phases

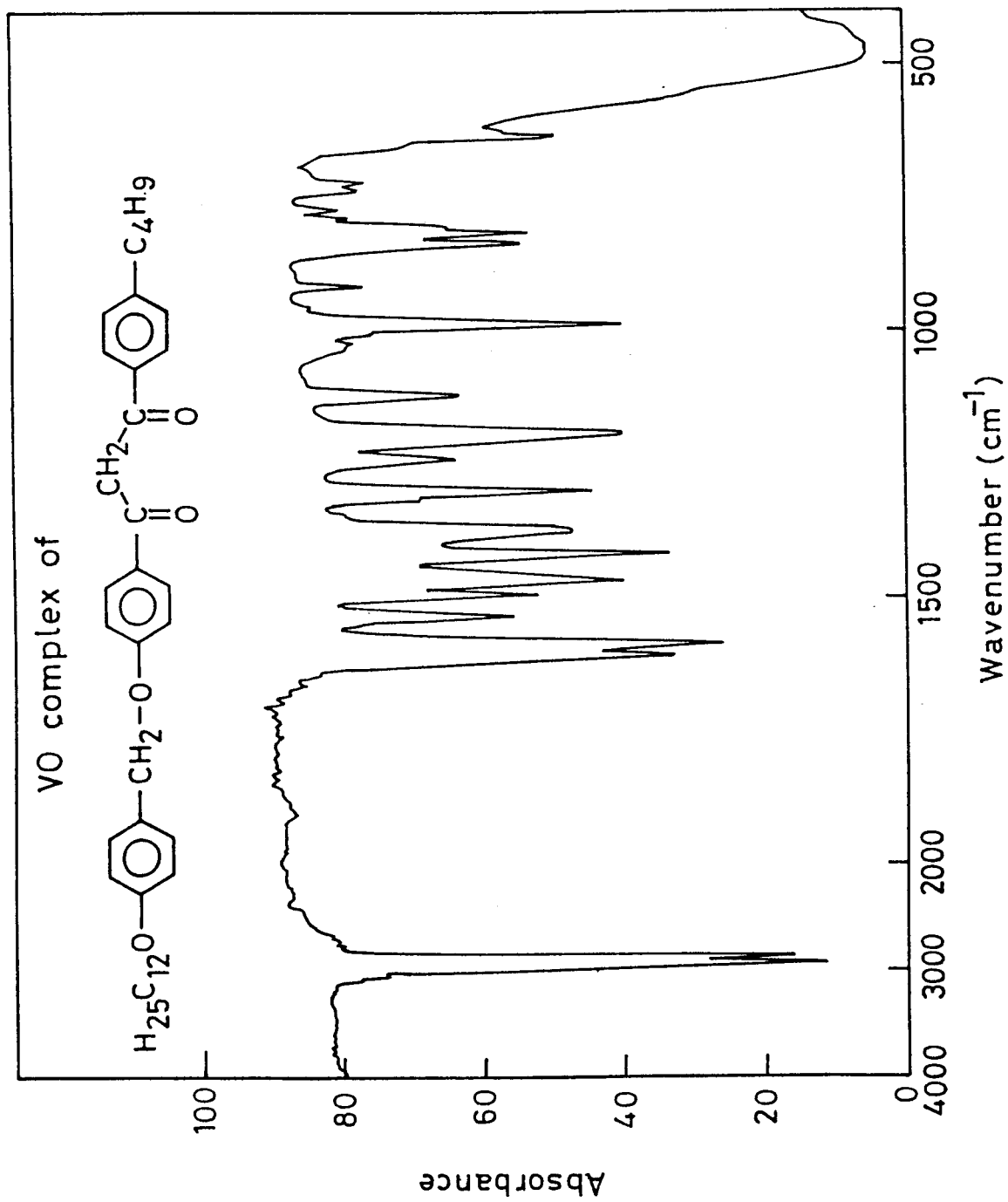
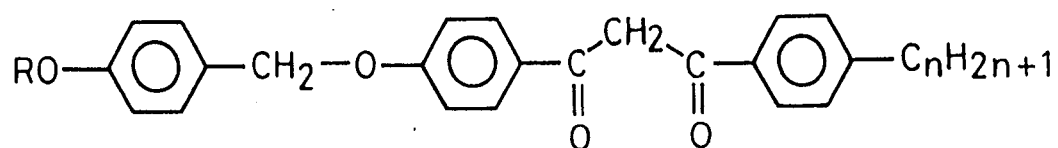


Fig.5.5. IR spectrum of compound 5.c.1

**Table 5.1**Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of**Series V(I)**

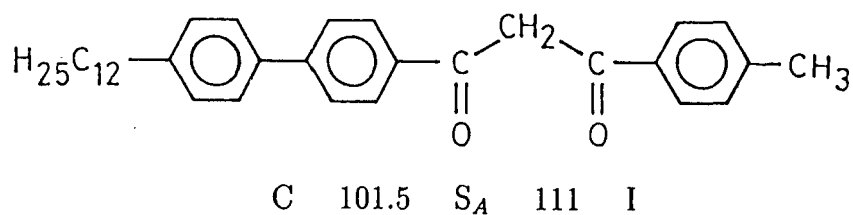
Compound number	R	n	C	$S_C$	$S_A$	I
5.a.1	$\text{C}_{12}\text{H}_{25}$	1	.	108.5 16.14	-	-
5.a.2	$\text{C}_{12}\text{H}_{25}$	4	.	85.5 12.40	-	89.0 1.53
5.a.3	$\text{C}_{12}\text{H}_{25}$	6	.	84.5 12.50	(. 80.0*)	91.0 1.63
5.a.4	$\text{C}_{12}\text{H}_{25}$	12	.	85.0 14.94	89.0*	92.5 1.88
5.a.5	$\text{C}_7\text{H}_{15}$	1	.	107.5 9.98	-	-
5.a.6	$\text{C}_7\text{H}_{15}$	4	.	88.0 7.81	-	(. 79.0) 0.86
5.a.7	$\text{C}_7\text{H}_{15}$	12	.	81.5 12.17	-	87.5 1.37
5.a.8	$\text{C}_2\text{H}_5$	10	.	87.5 9.42	-	-
5.a.9	$\text{C}_2\text{H}_5$	12	.	89.5 11.17	-	-

\*The enthalpy of transition could not be accurately determined.

respectively. The mesophase range varies from 3.5 to 7.5°C in this series. Higher homologues show mesophase thermal stability and S<sub>A</sub>-I temperature increases as the alkyl chain is lengthened. An examination of compounds 5.a.5 to 5.a.7, i.e., a series of [1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-alkylphenyl)propane]-1,3-diones shows that the lowest homologue (5.a.5) is non-mesogenic. The butyl derivative (5.a.6) exhibits smectic A phase and this phase is retained in the dodecyl derivative (5.a.7). No other mesophase except S<sub>A</sub> is found in this series. As the alkyl chain is lengthened the melting point decreases and the mesophase range increases. The magnitude of the enthalpies of various phase transitions in all these mesogenic compounds are similar to those that have been determined for such transitions in other calamitic compounds.

A comparison of the mesogenic properties of compounds 5.a.4, 5.a.7 and 5.a.9 shows that in the case of compound 5.a.4, the thermal range of smectic phase is 7.5°C. It exhibits S<sub>A</sub> and S<sub>C</sub> phases, whereas compound 5.a.7 exhibits only a smectic A phase with 6°C thermal range. However, compound 5.a.9 does not exhibit any mesophase. The behaviour of these three derivatives reveals that as the length of alkoxy chain on benzyloxyphenyl moiety is shortened, the mesophase thermal stability decreases and when the chain length is very small (in compound 5.a.9) the mesogenicity of the compound disappears. Thus short chains on the benzyloxyphenyl group do not enhance mesogenic properties.

A comparison of the mesogenic behaviour of 1-(4-n-dodecylbiphenyl)-3-(4''-methylphenyl)propane-1,3-dione (5.6) with compound 5.a.1 shows the effect of the methyleneoxy linkage group.

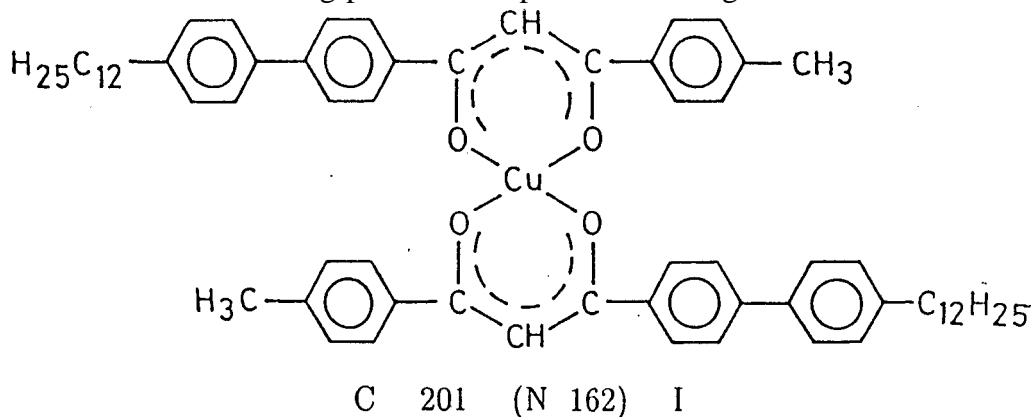


### 5.6

Compound 5.6 exhibits an enantiotropic smectic A phase and has a clearing temperature at  $110^{\circ}\text{C}$ . However, no mesogenic behaviour was found in compound 5.a.1; this is perhaps due to non-linear structure of the latter, which is not favourable for efficient packing. However, as expected the melting point is lowered in compound 5.a.1. An examination of the Dreiding stereomodels for compounds 5.a.1 and 5.6 shows clearly the effect of introduction of a methyleneoxy group.

The thermal behaviour and the calorimetric data for the bis[1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-alkylphenyl)propane-1,3-dionato]copper(II) complexes are summarised in table 5.2. All the compounds are non-mesogenic. The melting points of these complexes are in the range of  $171^{\circ}\text{C}$  to  $199^{\circ}\text{C}$ .

If we compare the thermal behaviour of bis[1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-methylphenyl)propane-1,3-dionato]copper(II) complexes, (5.b.1) with bis[1-(4-n-dodecylbiphenyl)-3-(4''-methylphenyl)propane-1,3-dionato]copper(II), (5.7) then it is observed that the melting point of compound 5.7 is higher than 5.b.1.



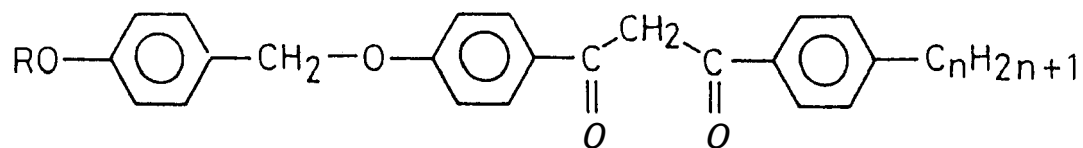
### 5.7

This indicates that probably the flexible methyleneoxy group lowers the melting point in compound 5.b.1. Compound 5.7 exhibits a monotropic nematic phase, while 5.b.1 is non-mesogenic. Thus the linearity of the molecule seems to play an important role for it to exhibit mesomorphism.

In order to study the effect of oxovanadium(IV) in place of a copper(II) atom, a few of the former complexes were synthesised. These complexes also do not exhibit

**Table 5.2**  
**Mesomorphic transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies (kcal/mol) of**

**Cu complex of**



**Series V(2)**

Compound number	R	n	C	I
5.b.1	C <sub>12</sub> H <sub>25</sub>	1	.	171.0 12.71
5.b.2	C <sub>12</sub> H <sub>25</sub>	4	.	177.5 15.10
5.b.3	C <sub>12</sub> H <sub>25</sub>	6	.	177.0 14.34
5.b.4	C <sub>12</sub> H <sub>25</sub>	12	.	171.5 17.18
5.b.5	C <sub>7</sub> H <sub>15</sub>	1	.	199.0 14.73
5.b.6	C <sub>7</sub> H <sub>15</sub>	4	.	194.0 14.73
5.b.7	C <sub>7</sub> H <sub>15</sub>	12	.	183.5 15.34
5.b.8	C <sub>2</sub> H <sub>5</sub>	10	.	188.0 13.88
5.b.9	C <sub>2</sub> H <sub>5</sub>	12	.	181.0 12.69

any mesogenic behaviour like their copper(II) congeners, except that the melting points of these complexes are lower. This is attributed to the square pyramidal arrangement of the chelate ring as compared to the square planar geometry of the copper(II) complexes.

Thus, we can conclude from the results obtained that the introduction of a methyleneoxy group in the above  $\beta$ -diketones affords compounds with lower melting and clearing temperatures as expected. However, in the metal complexes the mesomorphism completely disappears probably due to the geometry of the structures of the resulting complexes. Further, the oxovanadium(IV) complexes have lower melting points as compared to their copper(II) congeners.



## 5.4 Experimental

### 4-n-Dodecyloxybenzylalcohol

This was synthesised following the Williamson ether synthesis.<sup>30</sup> Thus, a mixture of 4-hydroxybenzylalcohol (5 g, 0.04 mol), n-dodecylbromide (12 g, 0.04 mol) and potassium carbonate (22 g, 0.16 mol) was stirred and refluxed in dry acetone for 24 hours. The reaction mixture was cooled and poured carefully into a mixture of ice-cold water (400 ml) and hydrochloric acid (50 ml). This was extracted with diethyl ether (3x100 ml). The combined ethereal extracts were washed with water (4x100 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of solvent afforded a product which was purified by crystallisation from petroleum ether.

Yield (8 g, 68%); m.p.  $66.5^\circ\text{C}$ ; IR  $\nu_{\text{max}}^{\text{nujol}}$  3300, 3200, 2900, 2850, 1620, 1580, 1520, 1460, 1380, 1250, 1170, 1040, 820  $\text{cm}^{-1}$ ; NMR  $\delta$  0.87 (t, 3H,  $\text{CH}_3$ ), 1.1-1.87 (m, 20H,  $10 \times \text{CH}_2$ ), 3.9 (t, 2H,  $-\text{OCH}_2$ ), 4.6 (s, 2H,  $\text{ArCH}_2$ ).

*Elemental analysis:* Found, C,78.13; H,11.29%  $\text{C}_{19}\text{H}_{32}\text{O}_2$  requires  
C,78.08; H,10.95%.

The physical data of the cognate preparations of other 4-n-alkoxybenzylalcohols are given below.

### 4-n-Ethoxybenzylalcohol

Yield 69%; b.p.  $90-95^\circ\text{C}/0.5$  mm; IR  $\nu_{\text{max}}^{\text{nujol}}$  3300, 3000, 2900, 2850, 1610, 1580, 1515, 1460, 1380, 1240, 1170, 1045, 820  $\text{cm}^{-1}$ ; NMR  $\delta$  1.4 (t, 3H,  $\text{CH}_3$ ), 3.6-4.1 (q, 2H,  $-\text{OCH}_2$ ), 4.4 (s, 2H,  $\text{ArCH}_2$ ), 6.5-7.3 (m, 4H,  $\text{ArH}$ ).

### 4-n-Heptyloxybenzylalcohol

Yield 60%; m.p.  $47.0^\circ\text{C}$ ; IR  $\nu_{\text{max}}^{\text{nujol}}$  3350, 3250, 2900, 2850, 1620, 1580, 1520, 1470, 1260, 1170, 1050, 820  $\text{cm}^{-1}$ ; NMR  $\delta$  0.9 (t, 3H,  $\text{CH}_3$ ), 1.1-2.1 (m, 10H,  $5 \times \text{CH}_2$ ), 3.9

(t, 2H, -OCH<sub>2</sub>), 4.5 (s, 2H, ArCH<sub>2</sub>), 6.6-7.4 (m, 4H, ArH).

*Elemental analysis:* Found, C,75.95; H,10.07% C<sub>14</sub>H<sub>22</sub>O<sub>2</sub> requires  
C,75.67; H, 9.90%.

#### **4-n-Decyloxybenzylbromide**

This was prepared following the standard procedure.<sup>31</sup> Thus,4-n-dodecyloxybenzyl alcohol (7.3 g, 24.96 mmol) was dissolved in dry carbon tetrachloride (50 ml) at room temperature and stirred magnetically. Phosphorus tribromide (3.37 g, 12.43 mmol) was added **dropwise** to the mixture. When addition was complete, the reaction mixture was warmed gently using an oil bath and the temperature of the oil bath was raised to 100°C and maintained at this temperature for twelve hours. Then the reaction mixture was allowed to cool, shaken with ether (500 ml) and filtered. The filtrate was washed with water (2x250 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of solvent afforded a pale yellow product which was distilled under reduced pressure.

Yield (7 g, 80%); b.p. 185-190°C/1.5 mm; IR  $\nu_{max}^{nujol}$  2900, 2850, 1620, 1520, 1470, 1250, 1180, 830 cm<sup>-1</sup>.

The boiling points and IR data of the cognate preparations of other 4-n-alkoxybenzylbromides are given below. These bromides are highly unstable, and hence the other analytical data could not be taken.

#### **4-Ethoxybenzylbromide**

Yield 58.4%; b.p. 90-95°C/3 mm; IR  $\nu_{max}^{neat}$  2900, 2850, 1620, 1515, 1470, 1180, 820 cm<sup>-1</sup>.

#### **4-n-Heptyloxybenzylbromide**

Yield 83.5%; b.p.135-140°C/0.7 mm; IR  $\nu_{max}^{nujol}$  2900, 2850, 1620, 1515, 1470, 1180, 830 cm<sup>-1</sup>.

### Ethyl (4-n-dodecyloxybenzyloxy)benzoate

A mixture of ethyl 4-hydroxybenzoate (1.41 g, 8.45 mmol), 4-n-dodecyloxybenzyl bromide (3 g, 8.45 mmol) and potassium carbonate (4.66 g, 33.76 mmol) was stirred and refluxed in dry butan-2-one for 12 hours. The reaction mixture was then cooled and poured carefully into a mixture of ice-cold water (300 ml) and hydrochloric acid (50 ml). This was extracted with diethyl ether (3x200 ml). The combined ethereal solution was washed with cold 10% sodium bicarbonate solution (2x75 ml), water (3x200 ml) and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent afforded a product which was purified by column chromatography and crystallised from petroleum ether.

Yield (3.5 g, 85.7%); m.p.  $65.5^\circ\text{C}$ ; IR  $\nu_{\text{max}}^{\text{nujol}}$  2900, 2850, 1710, 1610, 1520, 1460, 1380, 840,  $770\text{ cm}^{-1}$ ; NMR  $\delta$  0.8 (t, 3H,  $\text{CH}_3$ ), 1.1-1.6 (m, 23H,  $10 \times \text{CH}_2 + \text{CH}_3$ ), 3.92 (t, 2H,  $-\text{OCH}_2$ ), 4.2-4.5 (q, 2H,  $\text{COO}-\text{CH}_2$ ), 5.05 (s, 2H,  $\text{OCH}_2$ ), 6.8-8.1 (m, 8H, ArH).

Elemental analysis: Found, C,75.85; H,9.41%  $\text{C}_{28}\text{H}_{40}\text{O}_4$  requires  
C,76.36; H,9.09%.

The physical data of the cognate preparations of other ethyl (4-n-alkoxybenzyloxy) benzoates are given below.

### Ethyl (4-ethoxybenzyloxy)benzoate

Yield 45%; m.p.  $120.0^\circ\text{C}$ ; IR  $\nu_{\text{max}}^{\text{nujol}}$  2900, 2850, 1710, 1605, 1520, 1460, 1385, 840,  $770\text{ cm}^{-1}$ ; NMR  $\delta$  1.25-1.68 (m, 6H,  $2 \times \text{CH}_3$ ), 3.87-4.18 (q, 2H,  $\text{ArOCH}_2$ ), 4.19-4.5 (q, 2H,  $\text{COOCH}_2$ ), 5 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.81-8.12 (m, 8H, ArH).

Elemental analysis: Found, C,71.79; H,6.73%  $\text{C}_{18}\text{H}_{20}\text{O}_4$  requires  
C,72.00; H,6.66%.

### **Ethyl (4-n-heptyloxybenzyloxy)benzoate**

Yield 56%; m.p.  $66.5^{\circ}\text{C}$ ; IR  $\nu_{\text{max}}^{\text{nujol}}$  2900, 2850, 1710, 1610, 1520, 1460, 1380, 840, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.96 (t, 3H,  $\text{CH}_3$ ), 1.2-2 (m, 13H,  $5 \times \text{CH}_2 + \text{CH}_3$ ), 3.9 (t, 2H,  $\text{ArOCH}_2$ ), 4.2-4.5 (q, 2H,  $\text{COOCH}_2$ ), 5 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.8-8.1 (m, 8H,  $\text{ArH}$ ).

**Elemental analysis:** Found, C,74.87; H,8.30%  $\text{C}_{23}\text{H}_{30}\text{O}_4$  requires  
C,74.59; H,8.10%.

### **n-Pentylphenyl ketone**

This was prepared following the well known procedure.<sup>32</sup> Thus, by Friedel-Crafts reaction using n-hexanoylchloride (80 g, 0.59 mol), benzene (400 ml) and anhydrous aluminium chloride (96 g, 0.72 mol), n-pentylphenyl ketone (85.5 g, 81%); b.p.  $100-103^{\circ}\text{C}/1$  mm was obtained. (Reported<sup>33</sup> b.p.  $95-100^{\circ}\text{C}/2$  mm, yield 60%).

The physical data for the other n-alkylphenyl ketones are given in table 5.3.

### **n-Hexylbenzene**

This was prepared by Huang-Minlon modification of Wolff-Kishner reduction of n-pentylphenyl ketone (85 g, 0.48 mol) using hydrazine hydrate 80% (48 ml, 0.78 mol), potassium hydroxide (64 g, 1.14 mol) and digol (480 ml). n-Hexylbenzene (54.5 g, 72.5%); b.p.  $86-88^{\circ}\text{C}/1$  mm was obtained. (Reported<sup>34</sup> b.p.  $220-225^{\circ}\text{C}/760$  mm).

The physical data of the cognate preparations of other n-alkylbenzenes are given in table 5.4.

### **4-n-Hexylacetophenone**

This was prepared from n-hexylbenzene (54 g, 0.35 mol), acetyl chloride (26 g, 0.33 mol), anhydrous aluminium chloride (54 g, 0.40 mol) and dry carbon disulphide (300

**Table 5.3**Physical data of R.CO.C<sub>6</sub>H<sub>5</sub>

R	Observed b.p.°C/mm	Yield %	Reference
n-C <sub>3</sub> H <sub>7</sub>	96-98°C/1	94	32
n-C <sub>9</sub> H <sub>19</sub>	140-145°C/2.5	75	33
n-C <sub>11</sub> H <sub>23</sub>	147.5°C/1	75	33

**Table 5.4**Physical data of R.C<sub>6</sub>H<sub>5</sub>

R	Observed b.p.°C/mm	Yield %	Reference
n-C <sub>4</sub> H <sub>9</sub>	181-183/690	90	34
n-C <sub>10</sub> H <sub>21</sub>	102-104/2	70	36
n-C <sub>12</sub> H <sub>25</sub>	138/1-2	80	37

ml) by following a procedure similar to the one described above for 1-pentylphenyl ketone.

Yield (45 g, 57.8%); b.p. 120-123°C/1 mm (Reported<sup>35</sup> b.p. 120°C/1 mm. Yield 90.5%).

The physical data of the cognate preparations of other 4-n-alkylacetophenones are given in table 5.5.

**[1-(4-n-Dodecyloxybenzyloxyphenyl)-3-(4''-methylphenyl)propane]  
-1,3-dione, (5.a.1)**

A mixture of ethyl-(4-n-dodecyloxybenzyloxy)benzoate (1.5 g, 3.40 mmol) and 4-methylacetophenone (0.45 g, 3.35 mmol) was dissolved in dry 1,2-dimethoxyethane (100 ml) in a 250 ml. round bottom flask under nitrogen. This was stirred magnetically and sodium hydride (80% suspension in paraffin oil, 0.2 g, 6.66 mmol) was added to it. The mixture was refluxed for four hours and left overnight at room temperature. The reaction flask was cooled in ice and ice-cold dilute hydrochloric acid (20 ml) was added carefully to the reaction mixture and the yellow stew obtained was extracted with diethyl ether (4×100 ml). The combined ethereal solution was washed with water (3×100 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent afforded a pale yellow material which was chromatographed on silica gel. The required compound so obtained was crystallised several times from petroleum ether until the transition temperatures were constant.

Yield (0.9 g, 50%); m.p. 107.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1590, 1460, 1380, 1180, 780 cm<sup>-1</sup>; NMR  $\delta$  0.9 (t, 3H, CH<sub>3</sub>), 1.13-1.68 (m, 20H, 10×CH<sub>2</sub>), 2.5 (s, 3H, ArCH<sub>3</sub>), 4 (t, 2H, ArOCH<sub>2</sub>), 5.1 (s, 2H, CH<sub>2</sub>O), 6.8-8.1 (m, 13H, ArH, +C=CH), 17 (s, 1H, enol OH).

*Elemental analysis:* Found, C, 79.13; H, 8.53% C<sub>35</sub>H<sub>44</sub>O<sub>4</sub> requires  
C, 79.54; H, 8.33%.

Table 5.5

Physical data of R.C<sub>6</sub>H<sub>4</sub>.COCH<sub>3</sub>

R	Observed b.p.°C/mm	Yield %	Reference
CH <sub>3</sub>	93-94/7	86	38
n-C <sub>4</sub> H <sub>9</sub>	96-98/1	60	35
n-C <sub>10</sub> H <sub>21</sub>	160-165/1	60	35
n-C <sub>12</sub> H <sub>25</sub>	205-207/2	70	35

**[1-(4-n-Dodecyloxybenzyloxyphenyl)-3-(4''-n-butylphenyl)propane]-  
1,3-dione, (5.a.2)**

Yield 48%; m.p. 85.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1585, 1460, 1370, 1255, 1180, 850, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.9 (t, 6H,  $2 \times \text{CH}_3$ ), 1.15-1.65 (m, 24H,  $12 \times \text{CH}_2$ ), 2.7 (t, 2H,  $\text{ArCH}_2$ ), 4 (t, 2H,  $\text{ArOCH}_2$ ), 5 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.75-8.18 (m, 13H,  $\text{ArH}$ , +  $\text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

Elemental analysis: Found, C,79.94; H,9.00%  $\text{C}_{38}\text{H}_{50}\text{O}_4$  requires  
C,80.00; H,8.77%.

**[1-(4-n-Dodecyloxybenzyloxyphenyl)-3-(4''-n-hexylphenyl)propane]-  
1,3-dione, (5.a.3)**

Yield 44%; m.p. 84.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1585, 1460, 1380, 1250, 1180, 775  $\text{cm}^{-1}$ ; NMR  $\delta$  0.95 (t, 6H,  $2 \times \text{CH}_3$ ), 1.18-1.77 (m, 28H,  $14 \times \text{CH}_2$ ), 2.68 (t, 2H,  $\text{ArCH}_2$ ), 4 (t, 2H,  $\text{ArOCH}_2$ ), 5 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.8-8.13 (m, 13H,  $\text{ArH}$ , +  $\text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

Elemental analysis: Found, C,79.94; H,9.12%  $\text{C}_{40}\text{H}_{54}\text{O}_4$  requires  
C,80.26; H,9.03%.

**[1-(4-n-Dodecyloxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl)propane]-  
1,3-dione, (5.a.4)**

Yield 45%; m.p. 85.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1590, 1460, 1370, 1255, 1180, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.85 (t, 6H,  $2 \times \text{CH}_3$ ), 1.2-1.8 (m, 40H,  $20 \times \text{CH}_2$ ), 2.7 (t, 2H,  $\text{ArCH}_2$ ), 4.0 (t, 2H,  $\text{ArOCH}_2$ ), 5.1 (s, 2H,  $-\text{CH}_2\text{O}$ ), 6.77-8.2 (m, 13H,  $\text{ArH}$ , +  $\text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

Elemental analysis: Found, C,80.72; H,9.92%  $\text{C}_{46}\text{H}_{66}\text{O}_4$  requires  
C,80.93; H,9.67%.



**[1-(4-n-Heptyloxybenzyloxyphenyl)-3-(4''-methylphenyl)propane]-  
1,3-dione, (5.a.5)**

This ~~was~~ synthesised from 4-methylacetophenone (1.3 g, 7.38 mmol), ethyl-(4-n-heptyloxybenzyloxy)benzoate (2.0 g, 7.40 mmol), dry 1,2-dimethoxyethane (150 ml) and sodium hydride (0.43 g, 14.58 mmol, 80% dispersed in oil) by following a similar procedure described for the synthesis of compound 5.a.1.

Yield (1.2 g, 32.5%); m.p. 107.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1585, 1460, 1250, 1170, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.9 (t, 3H,  $\text{CH}_3$ ), 1.2-1.75 (m, 10H,  $5 \times \text{CH}_2$ ), 2.4 (s, 2H,  $\text{ArCH}_2$ ), 4.0 (t, 2H,  $\text{ArOCH}_2$ ), 5 (s, 2H,  $-\text{CH}_2\text{O}$ ), 6.7-8.2 (m, 13H,  $\text{ArH}$ ,  $\dagger \text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

Elemental analysis: Found, C,77.23; H,9.30%  $\text{C}_{30}\text{H}_{44}\text{O}_4$  requires  
C,76.92; H,9.40%.

The physical data of the cognate preparations of other [1-(4-n-heptyloxybenzyloxy phenyl)-3-(4''-alkylphenyl) propane]-1,3-diones are given below.

**[1-(4-n-Heptyloxybenzyloxyphenyl)-3-(4''-n-butylphenyl)propane]-  
1,3-dione, (5.a.6)**

Yield 35%; m.p. 88.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1585, 1460, 1380, 1260, 1170, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.85 (t, 6H,  $2 \times \text{CH}_3$ ), 1.2-1.75 (m, 14H,  $7 \times \text{CH}_2$ ), 2.7 (t, 2H,  $\text{ArCH}_2$ ), 3.9 (t, 2H,  $\text{ArOCH}_2$ ), 5.1 (s, 2H,  $-\text{CH}_2\text{O}$ ), 6.8-8.1 (m, 13H,  $\text{ArH}$ ,  $\dagger \text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

Elemental analysis: Found, C,79.49; H,8.11%  $\text{C}_{33}\text{H}_{40}\text{O}_4$  requires  
C,79.20; H,8.00%.

**[1-(4-n-Heptyloxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl)propane]-  
1,3-dione, (5.a.7)**

Yield 35%; m.p. 81.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1585, 1460, 1370, 1250, 1180, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.85 (t, 3H,  $\text{CH}_3$ ), 1.15-1.8 (m, 30H, 15 x  $\text{CH}_2$ ), 2.7 (t, 2H,  $\text{ArCH}_2$ ), 4 (t, 2H,  $\text{ArOCH}_2$ ), 5 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.75-8.1 (m, 13H,  $\text{ArH}$ ,  $\text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

*Elemental analysis:* Found, C,80.44; H,9.37%  $\text{C}_{41}\text{H}_{56}\text{O}_4$  requires  
C,80.39; H,9.15%.

**[1-(4-Ethoxybenzyloxyphenyl)-3-(4''-n-decylphenyl)propane]-  
1,3-dione, (5.a.8)**

This was prepared from 4-n-decylacetophenone (1 g, 3.84 mmol), ethyl (4-ethoxybenzyloxy)benzoate (1.1 g, 3.81 mmol), dry 1,2-dimethoxyethane (100 ml) and sodium hydride (0.22 g, 7.5 mmol, 80% dispersed in oil) by following a procedure similar to the one described for the synthesis of compound 5.a.1.

Yield (0.8 g, 80%); m.p. 87.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1580, 1460, 1380, 1240, 1180, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.85 (t, 6H, 2 x  $\text{CH}_3$ ), 1.2-1.8 (m, 16H, 8 x  $\text{CH}_2$ ), 2.7 (t, 2H,  $\text{ArCH}_2$ ), 3.85-4.2 (q, 2H,  $\text{ArOCH}_2$ ), 5.01 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.7-8.1 (m, 13H,  $\text{ArH}$ ,  $\text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

*Elemental analysis:* Found, C,79.99; H,8.35%  $\text{C}_{34}\text{H}_{42}\text{O}_4$  requires  
C,79.37; H,8.17%.

**[1-(4-Ethoxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl)propane]-  
1,3-dione, (5.a.9)**

Yield 40%; m.p. 89.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1605, 1580, 1460, 1380, 1240, 1180, 780  $\text{cm}^{-1}$ ; NMR  $\delta$  0.85 (t, 6H, 2 x  $\text{CH}_3$ ), 1.15-1.9 (m, 20H, 10 x  $\text{CH}_2$ ), 2.9 (t, 2H,  $\text{ArCH}_2$ ), 3.9-4.2 (q, 2H,  $\text{ArOCH}_2$ ), 5.01 (s, 2H,  $\text{CH}_2\text{O}$ ), 6.75-8.1 (m, 13H,  $\text{ArH}$ ,  $\text{C}=\text{CH}$ ), 17 (s, 1H, enol OH).

C=CH), 17 (s, 1H, enol OH).

*Elemental analysis:* Found, C,79.20; H,8.59% C<sub>46</sub>H<sub>66</sub>O<sub>4</sub> requires  
C,79.70; H,8.48%.

**Bis[1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-methylphenyl)propane-1,3-dionato] copper(II), (5.b.1)**

A solution of potassium hydroxide (0.023 g, 0.41 mmol) in ethyl alcohol (10 ml) was added to a rapidly stirred solution of 1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-methylphenyl) propane-1,3-dione (0.17 g, 0.33 mmol) in warm ethyl alcohol (20 ml). To this was added a solution of cupric chloride dihydrate (0.028 g, 0.164 mmol) in ethanol (10 ml). The mixture was stirred at room temperature for four hours. The green precipitate so obtained was collected and dissolved in chloroform (50 ml), washed with water (2x25 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of solvent afforded a green residue which was crystallised several times from butan-2-one.

Yield (0.08 g, 41%); m.p. 171.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1590, 1460, 1380, 1180, 780 cm<sup>-1</sup>; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 276 (41,500), 304 (42,500), 357.5 (74,300).

*Elemental analysis:* Found, C,75.44; H,7.79% C<sub>70</sub>H<sub>86</sub>O<sub>8</sub>Cu requires  
C,75.16; H,7.69%.

The physical data of the cognate preparations of other bis[1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-n-alkylphenyl)propane-1,3-dionato]copper(II) complexes are given below.

**Bis[1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-n-butylpropane-phenyl)1,3-dionato]copper(II), (5.b.2)**

Yield 35%; m.p. 177.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1584, 1460, 1380, 1180, 780 cm<sup>-1</sup>; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 276 (41,000), 302 (44,000), 357.5 (74,700).

*Elemental analysis:* Found, C,76.42; H,8.31%  $C_{76}H_{98}O_8Cu$  requires  
C,75.90; H,8.15%.

**Bis[1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-n-hexylphenyl) propane-  
1,3-dionato]copper(II), (5. b.3)**

Yield 35%; m.p.177.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1590, 1460, 1380, 1180, 780  $cm^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 276 (40,100), 303 (41,500), 357.5 (71,100).

*Elemental analysis:* Found, C,75.61; H,8.59%  $C_{80}H_{106}O_8Cu$  requires  
C,76.34; H,8.42%.

**Bis[1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl) propane-  
1,3-dionato]copper(II), (5.b.4)**

Yield 30%; m.p. 171.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1590, 1460, 1380, 1170, 780  $cm^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 276 (42,000), 304 (42,000), 357.5 (72,000).

*Elemental analysis:* Found, C,77.62; H,9.08%  $C_{92}H_{130}O_8Cu$  requires  
C,77.44; H,9.11%.

**Bis[1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-methylphenyl) propane-  
1,3-dionato]copper(II), (5. b.5)**

This complex was prepared from 1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-methyl phenyl)propane]-1,3-dione (0.22 g, 0.48 mmol), cupric chloride dihydrate (0.041 g, 0.24 mmol), potassium hydroxide (0.033 g, 0.59 mmol) and ethyl alcohol (50 ml) by following a procedure similar to the one described for the synthesis of compound 5.b.1.

Yield (0.12 g, 47%); m.p. 199.0°C; IR  $\nu_{max}^{nujol}$  2908, 2850, 1610, 1585, 1460, 1380, 1250, 1170, 780  $cm^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 275.4 (36,600), 302 (39,000), 357 (69,700).

*Elemental analysis:* Found, C,73.34; H,6.86%  $C_{60}H_{66}O_8Cu$  requires

C,73.65; H,6.75%.

**Bis[1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-n-butylphenyl) propane-1,3-dionato]copper(II), (5. b.6)**

Yield 35%; m.p. 194.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1590, 1460, 1350, 1240, 1180, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 276 (36,500), 302 (39,200), 357 (70,400).

Elemental analysis: Found, C,74.16; H,7.44%  $\text{C}_{66}\text{H}_{78}\text{O}_8\text{Cu}$  requires  
C,74.60; H,7.34%.

**Bis[1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl) propane-1,3-dionato]copper(II), (5. b.7)**

Yield 45%; m.p. 183.5°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1590, 1460, 1380, 1240, 1180, 780  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 275 (39,500), 304.5 (41,800), 357 (74,800).

Elemental analysis: Found, C,76.41; H,8.73%  $\text{C}_{82}\text{H}_{110}\text{O}_8\text{Cu}$  requires  
C,76.54; H,8.55%.

**Bis[1-(4-ethoxybenzyloxyphenyl)-3-(4''-n-decylphenyl) propane-1,3-dionato]copper(II), (5.b.8)**

This complex was prepared from [1-(4-ethoxybenzyloxyphenyl)-3-(4''-n-decylphenyl) propane]-1,3-dione (0.33 g, 0.64 mmol), cupric chloride dihydrate (0.054 g, 0.316 mmol), potassium hydroxide (0.045 g, 0.8 mmol) and ethyl alcohol (50 ml) by following a procedure similar to the one described for the synthesis of compound 5.b.1. Yield (0.14 g, 40%); m.p. 188.0°C; IR  $\nu_{max}^{nujol}$  2950, 2875, 1618, 1590, 1530, 1465, 1385, 1305, 1250, 1180, 785  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 275.5 (39,400), 301.6 (41,600), 357 (72,000).

Elemental analysis: Found, C,74.78; H,7.51%  $\text{C}_{34}\text{H}_{42}\text{O}_4$  requires  
C,74.89; H,7.52%.

**Bis[1-(4-ethoxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl) propane-1,3-dionato]copper(II), (5.b.9)**

Yield 37%; m.p. 181.0°C; IR  $\nu_{max}^{nujol}$  2950, 2875, 1618, 1590, 1530, 1465, 1385, 1305, 1250, 1180, 785  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  (c) 275 (39,500), 304.5 (41,800), 357.5 (74,800).

Elemental analysis: Found, C,75.73; H,7.85%  $\text{C}_{36}\text{H}_{46}\text{O}_4$  requires  
C,75.42; H,7.85%.

**Bis[1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-n-butylphenyl)propane-1,3-dionato]oxovanadium(IV), (5.c.1)**

To a stirred warm solution of [1-(4-n-dodecyloxybenzyloxyphenyl)-3-(4''-n-butylphenyl)propane]-1,3-dione (0.15 g, 0.26 mmol) in ethyl alcohol (50 ml) was added a solution of vanadyl sulphate pentahydrate (0.034 g, 0.13 mmol) in water (5 ml). To this greenish solution was added sodium acetate (0.045 g, 0.54 mmol) in water (5 ml). The resulting mixture was stirred and refluxed for twenty minutes and allowed to stand at room temperature for two hours. The green precipitate so obtained was filtered off, washed with water, ethyl alcohol and ether. This was crystallised several times from a mixture of chloroform-ethyl alcohol.

Yield (0.1g, 30%); m.p. 137.0°C; IR  $\nu_{max}^{nujol}$  2900, 2850, 1610, 1590, 1250, 990  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  (E) 277.5 (33,000), 309.5 (28,700), 369.5 (82,000), 398.5(36,650).

Elemental analysis: Found, C,75.83; H,8.34%  $\text{C}_{76}\text{H}_{98}\text{O}_9\text{V}$  requires  
C,75.68; H,8.13%.

The physical data of the cognate preparations of other bis[1-(4-n-alkoxybenzyloxyphenyl)-3-(4''-n-alkylphenyl) propane-1,3-dionato]oxovanadium(IV) complexes are given below.

**Bis[1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-n-dodecylphenyl) propane-1,3-dionato]oxovanadium(IV), (5.c.2)**

Yield 35%; m.p. 172.0°C; IR  $\nu_{max}^{nujol}$  2900,2850, 1605, 1585, 1240, 990  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 277 (32,900), 309.5 (28,730), 369.5 (81,900), 398.5(36,600).

Elemental analysis: Found, C,75.99; H,8.56%  $\text{C}_{82}\text{H}_{110}\text{O}_9\text{V}$  requires  
C,76.34; H,8.53%.

**Bis[1-(4-n-heptyloxybenzyloxyphenyl)-3-(4''-n-butylphenyl) propane-1,3-dionato]oxovanadium(IV), (5.c.3)**

Yield 30%; m.p. 160.5°C; IR  $\nu_{max}^{nujol}$  2900,2850, 1610, 1585, 1250, 985  $\text{cm}^{-1}$ ; UV-Vis  $\lambda_{max}^{CHCl_3}$  ( $\epsilon$ ) 279.5 (28,500), 309 (25,000), 374 (63,000), 397.5(39,000).

Elemental analysis: Found, C,74.57; H,7.07%  $\text{C}_{66}\text{H}_{78}\text{O}_9\text{V}$  requires  
C,74.37; H,7.32%.

## References

- [1] H.Kelker and B.Scheurle, *Angew. Chem.*, 81, 903 (1969).
- [2] J.S.Dave and P.R.Patel, *Mol. Cryst.*, 2, 103 (1966); *ibid*, 2, 115 (1966).
- [3] G.W.Smith, Z.G.Gardlund and R.J.Curtis, *Mol. Cryst. Liquid Cryst.*, 19, 327 (1973).
- [4] J. van der Veen, W.H. de Jeu, A.H.Grobbe and J.Boven, *Mol. Cryst. Liquid Cryst.*, 17, 291 (1972).
- [5] L.E.Knaak, H.M.Rosenberg and M.P.Serve, *Mol. Cryst. Liquid Cryst.*, 17, 171 (1972).
- [6] C.Weygand and R.Gabler, *J. Prakt. Chem.*, 155, 332 (1940).
- [7] W.R.Young, A.Aviram and R.J.Cox, *J. Am. Chem. Soc.*, 94, 3976 (1972).
- [8] R.J.Cox and M.J.Clecak, *Mol. Cryst. Liquid Cryst.*, 37, 263 (1976); *ibid*, 51, 209 (1979).
- [9] G.W.Gray and A.Mosley, *Mol. Cryst. Liquid Cryst.*, 37, 157 (1976).
- [10] W.R.Young, *Mol. Cryst. Liquid Cryst.*, 10, 237 (1970).
- [11] L.Richter, N.K.Sarma, R.Skubatz, D.Demus and H.Sackmann, *Mol. Cryst. Liquid Cryst.*; 80, 195 (1982).
- [12] R.E.Rondeau, M.A.Berwick, R.N.Steppel and M.P.Serve, *J. Am. Chem. Soc.*, 94, 1069 (1972).
- [13] G.W.Gray and A.Mosley, *Mol. Cryst. Liquid Cryst.*, 37, 213 (1976).
- [14] R.J.Cox and N.J.Clecak, *Mol. Cryst. Liquid Cryst.*, 37, 214 (1976).
- [15] J.Malthete, J.Canceill, J.Gabard and J.Jacques, *Tetrahedron*, 37, 2815 (1981).



- [16] H.J.Deutsche, F.Kuschel, S.König, H.Kresse, D.Pfeiffer, A.Wiegeleben, J.Wulf and D.Demus, *Z. Chem.*, 17, 64 (1977).
- [17] G.W.Gray and S.M.Kelly, *J. Chem. Soc. Chem. Commun.*, 465 (1980).
- [18] G.W.Gray and S.M.Kelly, *Mol. Cryst. Liquid Cryst.*, 75, 95 (1981).
- [19] G.W.Gray and S.M.Kelly, *Mol. Cryst. Liquid Cryst.*, 95, 101 (1983).
- [20] G.W.Gray and M.G.McDonnell, *Mol. Cryst. Liquid Cryst.*, 53, 147 (1979).
- [21] N.Carr and G.W.Gray, *Mol. Cryst. Liquid Cryst.*, 124, 27 (1985).
- [22] M.A.Osman, *Mol. Cryst. Liquid Cryst.*, 72, 291 (1982).
- [23] G.W.Gray, in *Advances in Liquid Crystals*, Vol.2, Ed. G.H.Brown (Academic Press, New York, 1976), p.11.
- [24] D.Demus, H.Demus and H.Zaschke, *Flussige Kristalle in Tabellen*, Vol.1 (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974),p.47.
- [25] D.Demus, H.Demus and H.Zaschke, *Flussige Kristalle in Tabellen*, Vol.1 (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974),p.114.
- [26] D.Demus, H.Demus and H.Zaschke, *Flussige Kristalle in Tabellen*, Vol.1 (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974),p.186.
- [27] D.Bruins and D.L.Weaver, *Inorg. Chem.*, 9, 130 (1970).
- [28] L.V.Bosa and J.C.Pessoa, *Comprehensive Coordination Chemistry*, Vol.3, Chapter 33, Ed. G.Wilkinson, R.Gillard, J.McCleavey (Pergamon Press, 1987).
- [29] A.Serrette, P.J.Carroll and T.M.Swager, *J. Am. Chem. Soc.*, 114, 1887 (1992).
- [30] A.W.Williamson, *J. Chem. Soc.*, 229 (1852).
- [31] *Organic Synthesis*, Collective Volume II, pp. 358-59 and 477.

- [32] A.I.Vogel, Textbook of Practical Organic Chemistry, (Longmans, Green and Co., London, 1971), p.732.
- [33] F.L.Breusch and M.Oguzer, Chem. Ber., 87, 1225 (1954).
- [34] A.I.Vogel, *Textbook of Practical Organic Chemistry*, (Longmans, Green and Co., London, 1971), p. 516.
- [35] C.G.Overberger, C.Frazier, J. Mandelman and H.Smith, J. Am. Chem. Soc., '75, 3326 (1953).
- [36] B.K.Sadashiva, Ph. D. Thesis, Bangalore University (1979), p.102.
- [37] Petrov and Lepteva, J. Gen. Chem. (USSR), 8, 207 (1938).
- [38] A.I.Vogel, Textbook of Practical Organic Chemistry, (Longmans, Green and Co., London, 1971), p. 776.