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D. Coates^a

^a STC Technology Limited, Harlow, Essex, England

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The influence of alkyl chain branching on smectic C formation

by D. COATES

STC Technology Limited, London Road, Harlow, Essex, CM17 9NA, England

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Fifty-five esters were prepared to show the effect of altering the point of alkyl chain branching on smectic C thermal stability. Six types of ester system were studied. Moving the position of alkyl chain branching away from the main molecular core enhanced smectic C thermal stability; after about the third carbon this effect was minimal. Extending the alkyl chain after the point of chain branching gradually lowered the smectic C thermal stability.

1. Introduction

In 1975 Meyer *et al.* [1] showed that the chiral smectic C phase (S_C^*) was ferroelectric. The technological importance of this discovery was realized when Clark and Lagerwall [2] demonstrated how an electro-optical device (surface stabilized ferroelectric liquid crystal, SSFLC), could be made by the action of a d.c. field upon the ferroelectric dipole moment. Since then there has been much more commercial and academic interest in the hitherto relatively unimportant smectic C phase.

The effect of molecular structure on the occurrence of the tilted smectic C phase is very different to that on the nematic or orthogonal smectic phases. Several theories for the occurrence of this tilted phase have been suggested and reviewed [3], and some generalizations as to what molecular features are essential or desirable have been suggested [4]. In very general terms one of the desirable features is that the molecule should possess some degree of steric asymmetry, so that when the molecules pack together they preferentially do so in a slightly displaced fashion, hence giving a tilted layer, i.e. molecules tilted within the layer. One way to achieve this is to branch a terminal alkyl chain. Although this is known to favour the formation of the smectic C phase relative to the *n*-alkyl chain analogues, the effect still requires some close comparative examination. Chain branching also provides the opportunity to use a chiral alkyl chain and thereby produce a chiral smectic C phase (S_C^*). Although this is not always essential, as it is often satisfactory to add an optically active dopant of high spontaneous polarization to a non-optically active host smectic C phase and thereby produce a mixture which is ferroelectric [5]. Nevertheless, this feature could be useful.

The aim of this work was to investigate how alkyl chain branching can help form smectic C phases, and to determine if there are any generalizations which might be incorporated in other molecular systems to enhance their smectic C properties. Various ester systems were used so that the environment of the branched alkyl chain could easily be altered.

As most commonly used branched alkyl groups are derived from readily available 2-methylbutanol, the examples here also use this as a source, hence 3-methylpentyl and 4-methylhexyl were used. In the cases where the alkyl chain has been extended

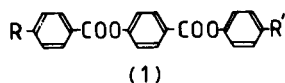
after the point of alkyl chain branching, the second carbon in the chain was used as the branching centre because it is analogous to the much studied 2-methylbutyl group, and these derivatives can readily be synthesized from diethyl malonate.

2. Results

2.1. Phenyl benzoyloxybenzoates (1)

The esters (1) [6(a, b)], their laterally substituted analogues [7] and some naphthalene derivatives [8] have been examined previously. The *n*-alkyl compounds were only weakly disposed to forming smectic C phases. Some branched chain homologues

Table 1. Temperatures of transition (in °C) for the 4-alkyl and 4-alkoxyphenyl 4'-alkyl- and 4'-alkoxy-benzoyloxybenzoates (1).



<i>R</i>	<i>R'</i>	C-S _C or N	S _C -S _A or N	S _A -N	N-I
2MB	C ₈ H ₁₇	74.2	—	—	132.4
4MH	C ₈ H ₁₇	84.0	84.4	—	132.4
2MB	C ₈ H ₁₇ O	75.6	(50.0)	—	155.7
4MH	C ₈ H ₁₇ O	95.3	(79.3)	—	168.7
2MBO	C ₈ H ₁₇	99.2	(60.0)	—	149.7
2MBO	C ₈ H ₁₇ O	82.7	99.3	—	151.1
4MH	2MB	90.3	—	—	121.4
C ₈ H ₁₇ O	C ₈ H ₁₇	85.0	86.9	160.3	173.9
C ₈ H ₁₇ O	2MB	93.0	100.4	136.4	169.0
C ₈ H ₁₇ O	3MP	86.6	109.6	151.6	164.8
C ₈ H ₁₇ O	4MH	78.2	101.5	149.6	162.2
C ₈ H ₁₇ O	2MBO	95.3	108.5	157.3	174.9
C ₁₀ H ₂₁	2MB	83.3	(77.1)	112.5	135.6

2MB = 2-methylbutyl; 3MP = 3-methylpentyl; 4MH = 4-methylhexyl.

have been reported [6(b)] but only cholesteric phases were reported for them. However the results presented here (cf. table 1) show that some of these compounds do exhibit smectic C phases. Several features can be seen from table 1.

- (1) When the branched alkyl or alkoxy chain is on the acid part of the molecule, smectic C–nematic transitions occur, while smectic C–smectic A followed by smectic A–nematic transitions occur when the branching centre is on the phenol part of the molecule.
- (2) Branching both ends of the molecule depresses the smectic C phase thermal stability considerably.
- (3) As is usual, alkoxy groups produce smectic C phases of higher thermal stability than do alkyl groups. An *n*-alkoxy group on the acid portion of the molecule gives a higher smectic C tendency than when it is on the phenol part of the molecule (of course, this may also be due to the change in position of the branched chain).
- (4) Branching the alkyl chain, compared to the *n*-octyl analogue (which usually promotes high smectic C thermal stability within an homologous series),

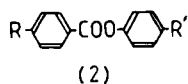
produces smectic C phases of increased thermal stability, this is particularly pronounced when the branched chain is on the phenol part of the molecule.

- (5) The effect of the type of chain branching also depends on where the branched chain is on the molecule. For instance, a 4-methylhexyl chain produces much more thermally stable smectic C phases than 2-methylbutyl when on the acid part of the molecule, but when the branched chain is on the phenol part of the molecule, smectic C phases of similar thermal stability are exhibited.

Because the smectic C phase occurs as an injected phase, usually at medium chain lengths within an homologous series, these results may not be as generally applicable as they would be for smectic A phases for instance. Some further examples of how chain branching in other esters compares in its effects to those found for the phenyl benzyloxybenzoates (**1**) are shown in the following systems.

2.2. Aromatic mono-esters

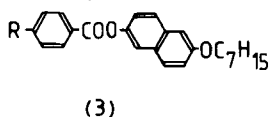
The well-known 4'-alkoxyphenyl 4-alkylbenzoates (**2**) produce smectic C phases [9], for example, when $R = C_8H_{17}O$; $R' = OC_5H_{11}$; C-S_C, 58°C; S_C-S_A, 64°C; S_A-N, 66°C; N-I, 85°C.



Branching the alkyl chain of R , in structure (**2**) lowers the smectic C thermal stability but lowers the melting point even more, and a low melting smectogen is produced [10], for example, $R = 4MHO$, $R' = C_7H_{15}O$; C-S_C, 34°C; S_C-N, 45.8°C; N-I, 62°C (where 4MHO = 4-methylhexyloxy). Other branched chain homologues did not show smectic C phases.

The naphthyl derivatives (**3**) were prepared as it was expected that they would have a higher smectic C thermal stability than the esters (**2**), thus allowing trends in smectic C formation to be examined. However, as the results in table 2 show, the melting points increased more than the thermal stability of the smectic C phase. This resulted in compounds where only the 4-methylhexyl and 4-methylhexyloxy homologues showed an enantiotropic smectic C phase, so the trends in smectic C formation could not be followed.

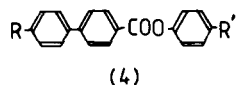
Table 2. Temperatures of transition (in °C) for 2-heptyloxy-6-naphthyl 4'-alkyl- and 4'-alkoxy-benzoates (**3**).



R	C-N	S _C -N	N-I
2MB	54.3		88.2
3MP	59.2		87.9
4MH	84.9	(~ 30)	88.8
2MBO	82.9		100.2
4MHO	63.6	(62.5)	113.0

2MB = 2-methylbutyl; 3MP = 3-methylpentyl; 4MH = 4-methylhexyl.

Table 3. Temperatures of transition (in °C) for 4-alkyl-phenyl 4'-alkyl- and 4'-alkoxy-biphenyl-4-carboxylates (4).



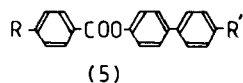
R	R'	C-S	S _J -S _I	S _I -S _C	S _C -S _A	S _A -N or I	N-I
C ₈ H ₁₇	2MB†	57	66.0	70.0	87.0	139.0	144.0 [11 (d)]
C ₈ H ₁₇	3MP	52.2	(39.9)	84.3	90.8	143.8	
C ₈ H ₁₇	4MH	66.0	—	82.8	92.8	138.5	
C ₈ H ₁₇	C ₇ H ₁₅	100.0	—	—	—	161.0	
C ₈ H ₁₇ O	2MB‡	74.0	(72.0)	79.0	132.0	171.0	174.0 [11 (d)]
C ₈ H ₁₇ O	3MP	85.1	(47.0)	95.9	144.6	177.2	
		C-S*				S _C -Ch	Ch-I
2MB	OC ₆ H ₁₃	68.8				80.2	168.5 [11 (b)]
4MH	OC ₆ H ₁₃	81.0				120.3	120.3 [11 (b)]

2MB = 2-methylbutyl; 3MP = 3-methylpentyl; 4MH = 4-methylhexyl.

† This compound also exhibits [22] an S_G-S_J transition at 64°C.

‡ This compound also exhibits [4] an S_K-S_J transition at 61°C.

Table 4. Temperatures of transition (in °C) for the 4-alkyl- and 4-alkoxy-4'-biphenyl 4-alkyl- and 4-alkoxy-benzoates (5).



R	R'	C-S _C	S _I -S _C	S _C -N	N-I	
C ₈ H ₁₇ O	2MB	78.9	—	100.2	160.6	
C ₈ H ₁₇ O	3MP	86.6	(69.9)	128.1	160.3	
		C-S	S _J -S _I	S _I -S _C	S _C -N	N-I
2MB	C ₁₀ H ₂₁ O	55.0	78.8	90.0	117.3	151.6
3MP	C ₁₀ H ₂₁ O	102.9	79.7	98.9	136.9	149.0
4MH	C ₁₀ H ₂₁ O	92.5	—	102.8	139.2	145.7
4MHO	C ₁₀ H ₂₁ O	111.1	—	(100)	152.3	166.6

2MB = 2-methylbutyl; 3MP = 3-methylpentyl; 4MH = 4-methylhexyl.

Biphenyl systems are well-known for increasing the thermal stability of liquid crystal phases relative to phenyl and naphthyl systems. The effect of using branched chains on some esters containing the biphenyl ring system has been reported for some 2-methylbutyl derivatives [11 (a-d)]. The phase behaviour of these and some further new compounds are given in tables 3 and 4. Several points can be seen from these results:

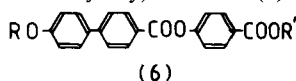
- (1) For the compounds in table 3, smectic C-smectic A transitions occur when the branched chain is on the phenol part of the molecule, otherwise smectic C-nematic transitions occur; this is similar to the results found for the phenyl benzyloxy benzoates (1). The esters in table 4 all show smectic C-nematic transitions, therefore the direction of the ester function is important. This feature has also been observed by Goodby *et al.* [4] in other systems.

- (2) The effect of moving the point of chain branching away from the aromatic core gives rise to a slight increase in the smectic C–smectic A transition temperature of the alkyl compounds shown in table 3, and a larger effect occurs for the alkoxy compounds. A more significant effect on the smectic C–nematic transition in the compounds listed in tables 3 and 4 occurs on moving from 2-methylbutyl to 3-methylpentyl and 4-methylhexyl. The *n*-alkyl analogues exhibit only smectic A phases; therefore, relative to the *n*-alkyl analogues, chain branching has increased smectic C thermal stability.
- (3) In compounds (4) (cf. table 3), higher-ordered smectic phases tend to occur more often when the branched chain is attached to the phenol moiety, rather than the biphenyl acid ring. In compounds (5) (cf. table 4) this is reversed and the branched alkyl chain on the benzoic acid moiety gives more thermally stable higher-ordered smectic phases.

2.3. Aromatic–alkyl diesters

The compounds (6) have been examined previously where $R = 2$ -methylbutyl [12] but only smectic C and smectic A phases were reported. The results for a wider range of alkyl chain branched compounds are shown in tables 5 and 6. In each case the denoted smectic I phase has been classified on the basis of its microscopic texture; although this has not been confirmed by miscibility or X-ray studies.

Table 5. Temperatures of transition (in °C) for the alkyl 4-(4-*n*-alkoxy-4'-biphenyl-carboxyloxy)benzoates (6).



R	R'	C–S	S_I – S_C	S_C – S_A	S_A –I
C_9H_{17}	1MP	71.0	(63.0)	136.0	174.5
C_8H_{17}	2MB	67.0	(61.5)	139.0	187.0
C_8H_{17}	3MP†	70.8	89.9	147.8	188.2
C_8H_{17}	4MH‡	77.7	88.2	138.2	182.6
$C_8H_{17}O$	2MP	74.6	(61.3)	138.3	183.0
$C_8H_{17}O$	2MH	60.9	(58.0)	135.0	179.0
$C_8H_{17}O$	2MO	66.0	(55.0)	121.4	171.8
$C_8H_{17}O$	2EH	72.2	(46.0)	122.3	151.3
C_5H_{11}	2MB	106.5	—	—	163.0

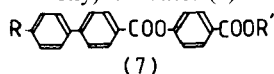
1MP = 1-methylpropyl; 2MB = 2-methylbutyl; 2MP = 2-methylpentyl; 3MP = 3-methylpentyl; 4MH = 4-methylhexyl; 2MH = 2-methylhexyl; 2MO = 2-methyloctyl; 2EH = 2-ethylhexyl.

† Another transition at 46° also occurs.

‡ Another transition at 55° also occurs.

In the first set of compounds in each table the spacing group between the point of alkyl chain branching and the ester function has been increased, and in the second group the alkyl chain after the point of alkyl chain branching has been extended. Several features can be seen from these results.

- (1) As the spacing group between the branched carbon and the carboxyl function increases, the smectic C thermal stability generally increases. A similar trend in the smectic I thermal stability also occurs.

Table 6. Temperatures of transition (in °C) for the alkyl 4-(4-*n*-alkyl-4'-biphenylcarbonyloxy)benzoates (7).

<i>R</i>	<i>R'</i>	C-S _C or S _I	S _I -S _C	S _C -S _A	S _A -I
C ₁₀ H ₂₁	1MP	61.0	(40.0)	81.5	102.5
C ₈ H ₁₇	2MB	68.9	(51.4)	103.6	154.5
C ₈ H ₁₇	3MP	67.4	75.7	107.2	153.9
C ₈ H ₁₇	4MH	58.5	72.3	107.7	148.5
C ₈ H ₁₇	2MP	57.2	(36.4)	93.7	150.4
C ₈ H ₁₇	2MH	54.5	(35.7)	91.7	145.0
C ₈ H ₁₇	C ₁₀ H ₂₁	86.2	—	—	149.8

1MP = 1-methylpropyl; 2MB = 2-methylbutyl; 3MP = 3-methylpentyl; 4MH = 4-methylhexyl; 2MH = 2-methylhexyl; 2MP = 2-methylpentyl.

- (2) Increasing the length of the alkyl chain after the point of chain branching gradually reduces the smectic C (and smectic I) thermal stability.
- (3) Smectic A–isotropic transitions are observed in all the esters; even the *R* = *n*-pentyl homologue in table 5 does not show a nematic phase, and the thermal stability of the smectic C phase falls dramatically as the chain length is decreased.
- (4) By increasing the branching chain from methyl to ethyl the thermal stability has fallen by 16°C, while the smectic A phase thermal stability has fallen much more (by 28.4°C).

3. Conclusion

From a study of these six ester systems some generalizations can be made regarding the effect of moving the point of alkyl chain branching at each end of the molecule.

3.1. When the branched alkyl chain is on the phenol or alcohol part of the ester

(a) Moving the branching centre away from the main molecular core aids smectic C thermal stability; this effect tends to level off after the third carbon, for example, 3-methylpentyl. The difference between 2MB and 4MH is usually between 6 and 18°C. Branching the chain beyond this occasionally raises the smectic C thermal stability, but less reliably.

(b) Extending the alkyl chain after the point of chain branching (in this case when the branching was at the second carbon) gradually lowers the smectic C thermal stability.

(c) Increasing the size of the branching group from methyl to ethyl lowers the smectic C thermal stability, but the smectic A thermal stability is reduced more.

(d) Smectic C–smectic A type transitions are often found, unless the phenol moiety is substantial, for example, biphenyl, then smectic C–nematic transitions occur. In these cases the effect of moving the branching centre away from the main core is usually substantial.

3.2. When the branched chain is on the acid moiety

(a) Moving the branching centre away from the main molecular core dramatically increases the smectic C thermal stability, 4MH > 3MP ≫ 2MB. The difference

between 2MB and 4MH is 30–40°C, most of which probably arises from the difference between 2MB and 3MP.

(b) All the mono-esters exhibited smectic C–nematic transitions while the diesters had smectic C–smectic A transitions. The preference of diesters to form smectic A phases has also been pointed out by Goodby and Leslie [10].

3.3. General effects

Smectic A thermal stability is not greatly influenced by the position of the alkyl chain branching. Alkoxy groups give higher smectic C (as well as smectic A and nematic) thermal stability than alkyl groups.

Branched alkyl chains on each end of the molecule depress smectic C thermal stability dramatically.

These observations relate to ester systems, for which they appear to hold reasonably well, indeed better than might be expected considering the very different types of ester examined. It is hoped that they will apply to non-esters as well.

4. Experimental

2-Methylbutyl bromide. Prepared by conventional bromination of racemic 2-methylbutanol.

3-Methylpentanoic acid. Prepared by carbonation [13] of the Grignard reagent from 2-methylbutyl bromide.

4-Methylhexanoic acid. Prepared by reaction of 2-methylbutyl bromide with diethylmalonate followed by hydrolysis of the diester and decarboxylation [13] of the resultant diacid.

3-Methylpentanol and 4-methylhexanol. Prepared by LiAlH_4 reduction [14] of 3-methylpentanoic acid and 4-methylhexanoic acid respectively.

3-Methylpentyl bromide and 4-methylhexyl bromide. Prepared by conventional bromination of the respective alcohols.

4-(2-Methylbutyl)-, 4-(3-methylpentyl)-, 4-(4-methylhexyl)- and 4-n-octyl-benzoyl chloride. Prepared by Friedel–Crafts acylation of benzene [13] followed by Huang–Minlon reduction to the alkylbenzene. Friedel–Crafts acylation of the alkylbenzene using oxalyl chloride [15] gave the required 4-alkylbenzoyl chloride.

4-(2-Methylbutyloxy)- and 4-(4-methylhexyloxy)-benzoic acids. Prepared by alkylation of 4-hydroxybenzoic acid [16]. These were then converted to the respective 4-alkyloxybenzoyl chlorides using oxalyl chloride.

4-(2-Methylbutyl)-, 4-(3-methylpentyl)-, 4-(4-methylhexyl)- and 4-n-heptyl-phenol. Prepared by Friedel–Crafts acylation [17] using the respective carboxylic acid chlorides on phenol, followed by Clemmenson reduction [18].

4-(2-Methylbutyloxy)- and 4-n-hexyloxy-phenol. Prepared by alkylation [19] of *p*-quinol using the appropriate alkyl bromides.

4-(2-Methylbutyl)- and 4-(3-methylpentyl)-4'-biphenol. Prepared by Friedel–Crafts acylation of 4-phenylphenol using the appropriate carboxylic acid chloride. Reduction of the carbonyl group gave the required products.

4-(2-Methylbutyl)-, 4-n-octyloxy-, 4-n-nonyl- and 4-n-octyl-biphenylcarboxylic acid chlorides. Prepared by acid hydrolysis of the corresponding 4-alkyl- or 4-alkoxy-4'-cyanobiphenyls to the free acid followed by conversion to the acid chloride using oxalyl chloride in benzene.

4-n-Decyloxy-4'-biphenol. Prepared by mono-alkylation of *p,p'*-biphenol [12].

6-Heptyloxy-2-naphthol. Prepared by mono-alkylation of 2,6-dihydroxynaphthalene [12].

4-Substituted phenyl 4-hydroxybenzoates. These were all prepared [20] from 4-hydroxybenzoic acid and the appropriate 4-substituted phenol using boric acid and sulphuric acid in toluene.

2-Methylpentanol, 2-methylhexanol and 2-methyloctanol. Prepared by alkylation of diethyl methylmalonate using *n*-propyl bromide, *n*-butyl bromide and *n*-hexyl bromide respectively. The resulting diethyl alkylmethylmalonate was hydrolysed to the diacid using alkali and then decarboxylated [13] to give 2-methylpentanoic acid, 2-methylhexanoic acid or 2-methyloctanoic acid respectively. These were then reduced with LiAlH_4 in ether to give the corresponding alcohols.

2-Ethylhexanol. Prepared as for the 2-methylalkanols but starting with diethyl ethylmalonate.

Alkyl 4-hydroxybenzoates. Due to the relatively small amounts of all the alcohols (except commercially available 2-methylbutanol) these esters were made by esterification of 4-benzyloxy benzoyl chloride and then debenylation [22] over Pd/C with hydrogen. The product was purified by column chromatography.

Esterification. All the esterifications were carried out by mixing the carboxylic acid chloride (0.01 m) with the respective alcohol or substituted phenol (0.11 m) in dry dichloromethane (30 ml) in the presence of triethylamine. The solution was stirred at room temperature for 16 hours. After washing with dilute acid and water, the product was purified by column chromatography on silica gel using various ratios of dichloromethane and petroleum ether. The ester was then crystallized at least once from ethanol or ethyl acetate until it was > 99.5 per cent pure (by HPLC) and gave constant sharp transition temperatures.

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References

- [1] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett., Paris*, **37**, 17.
- [2] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**(1), 899.
- [3] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals* (Leonard Hill), Chap. 3.
- [4] GOODBY, J. W., and LESLIE, T. M., 1984, *Molec. Crystals liq. Crystals*, **110**, 175.
- [5] BERESNEV, L. A., BAIKALOV, V. A., and BLINOV, L. M., *Soviet Phys. tech. Phys.*, **27**, 1296.
- [6] (a) STEINSTRÄSSER, R., 1972, *Angew. Chem.*, **84**, 636. (b) HSU, Y. Y., 1977, *Molec. Crystals liq. Crystals*, **42**, 1273.
- [7] VAN METER, J. P., and KLANDERMAN, B. H., 1973, *Molec. Crystals liq. Crystals*, **22**, 285. YOUNG, W. R., HALLER, I., and GREEN, D. C., 1972, *J. org. Chem.*, **37**, 3707.
- [8] COATES, D., and GRAY, G. W., 1978, *Molec. Crystals liq. Crystals*, **41**, 119.
- [9] DEMUS, D., DEMUS, I. H., and ZASCHKE, H., 1974, *Flüssige Kristalle in Tabellen*, (VEB).
- [10] GOODBY, J. W., and LESLIE, T. M., 1984, *Liq. Crystals Ordered Fluids*, **4**, 1.
- [11] (a) GOODBY, J. W., and GRAY, G. W., 1979, *J. Phys., Paris*, Coll. C3, **40**, 27. (b) GRAY, G. W., and McDONNELL, D. G., 1976, *Molec. Crystals liq. Crystals*, **37**, 157. (c) GRAY, G. W., and McDONNELL, D. G., 1978, *Molec. Crystals liq. Crystals*, **48**, 37. (d) GOODBY, J. W., and GRAY, G. W., 1978, *Molec. Crystals liq. Crystals*, **41**, 145.
- [12] EP0110299. Publ. 1984, Hitachi Ltd.
- [13] FURNISS, B. S., HANNAFORD, A. J., ROGERS, V., SMITH, P. W. G., and TACHELL, A. R., 1978, *Vogels Textbook of Practical Organic Chemistry* (Longman).

- [15] REYNOLDS, R. M., MAZE, C., and OPPENHEIM, E., 1976, *Molec. Crystals liq. Crystals*, **36**, 41.
- [16] GRAY, G. W., and JONES, B., 1954, *J. chem. Soc.*, p. 678.
- [17] CLOSE, W. J., TIFFANY, B. D., and SPILEMAN, M. A., 1949, *J. Am. chem. Soc.*, **71**, 1265.
- [18] READ, R. R., and WOOD, J., 1955, *Org. Syn. Coll.*, **3**, 444.
- [19] KLARMAN, E., GATYAS, L. W., and SHTERNOV, V. A., 1932, *J. Am. chem. Soc.*, **54**, 298.
- [20] LOWRANCE, W. W., 1971, *Tetrahedron Lett.*, p. 3453.
- [21] FREIFELDER, M., 1978, *Catalytic Hydrogenation in Organic Synthesis* (John Wiley).
- [22] BUDAI, J., PINDAK, R., DAVEY, S. C., and GOODBY, J. W., 1984, *J. Phys. Lett. Paris*, **45**, L1053.