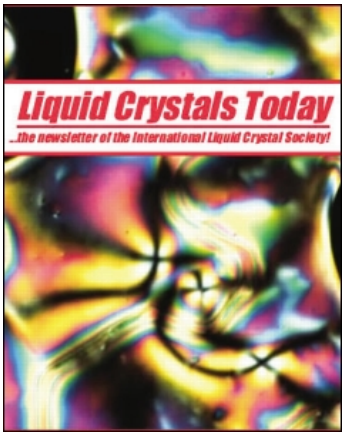

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Preliminary communication: The synthesis of new mesogenic 1,3,4-thiadiazole-2-carboxylate esters via a novel ring-closure

Patrick Bradley[a]; Paul Sampson[a]; Alexander J. Seed[a]
[a] Department of Chemistry, Kent State University, Kent, OH 44242-0001

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Preliminary communication: The synthesis of new mesogenic 1,3,4-thiadiazole-2-carboxylate esters via a novel ring-closure

PATRICK BRADLEY, PAUL SAMPSON and ALEXANDER J. SEED
Department of Chemistry, Kent State University, Kent, OH 44242-0001, USA

Two new 5-substituted 1,3,4-thiadiazole-2-carboxylate esters have been synthesized via ring closure of appropriate tricarbonyl precursors using Lawesson's reagent. The chemistry described is the first report of such methodology in the organic literature. The new materials display broad smectic C phases and show considerable potential for use in electrooptic display devices.

1. Introduction

A survey of the liquid crystal literature reveals that a large number of mesogenic 1,3,4-thiadizoles have been synthesized, although the chemical structures of these materials show very little variation. Substituents that have been incorporated at the 2- and 5- positions of the 1,3,4-thiadiazole ring include: (a) two aryl units, (b) an alkyl (or cycloalkyl) and an aryl unit, (c) two cycloalkyl units, (d) an alkyl and an amino-based unit (azo, amide or Schiff's base), (e) a perfluoroalkyl and an aryl unit and (f) an aryl and an amino unit (azo, amide or Schiff's base). Examples of such mesogens [1–10] are shown in figure 1 (**I**–**V**).

This lack of structural variation is clearly related to the ease of synthesis of these units and the limitations of synthetic methodology in the literature. 1,3,4-Thiadiazoles substituted at the 2- and 5-positions with alkyl, cycloalkyl and aryl units are typically synthesized by the cyclization of diacylhydrazides (**VI**) using a source of sulphur such as phosphorus pentasulphide or Lawesson's reagent (figure 2) [11].

1,3,4-Thiadiazoles with nitrogen-based linkers (amides, Schiff's bases or azo groups) at the 2-position have been recently synthesized by Parra and co-workers [6–10]. These materials are derived from 2-amino-1,3,4-thiadiazoles that are obtained via cyclization of the requisite thiosemicarbazides using either sulphuric acid or acetyl chloride in combination with HCl.

In order to synthesize 1,3,4-thiadiazoles that are more thermally and/or photochemically stable and are more conducive [12, 13] to smectic C phase formation, we have developed a new methodology for the preparation of 1,3,4-thiadiazole-2-carboxylate esters.

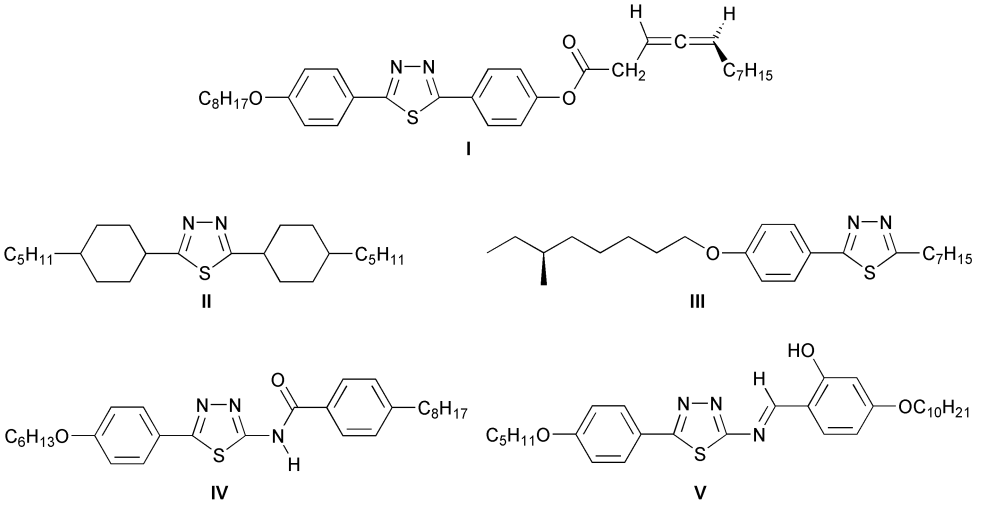

Figure 1. Typical mesogenic 1,3,4-thiadiazoles that have been reported in the literature.

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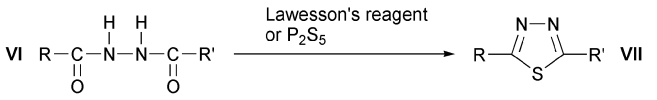


Figure 2. Cyclization of diacylhydrazides to give 1,3,4-thiadiazoles.

In 1982 Tanaka et al. reported the cyclization of ethoxalylaminoacetophenone (**VIII**) with phosphorus pentasulphide to give ethyl 5-phenyl-2-thiazolecarboxylate (**IX**) (figure 3) [14].

We postulated that analogous ethyl oxalyl diazanes might be cyclized to give 1,3,4-thiadiazole-2-carboxylate esters under similar conditions. Instead of using phosphorus pentasulphide as a source of sulphur we chose Lawesson's reagent [11] due to its greater reliability and ease of workup. Once cyclized, we expected to be able to saponify the esters and esterify the resulting carboxylate salts with appropriate phenols to give the desired target materials.

2. Synthetic discussion

The synthetic schemes used to prepare the two target materials (**7** and **13**) are shown below (Schemes 1 and 2).

The preparation of **2** utilized the standard Williamson ether synthesis [15]. Hydrazides **3** and **9** were obtained by reaction of esters **2** and **8** respectively with hydrazine in ethanol [16]. Synthesis of the ethyl oxalyl diazanes **4** and **10** was accomplished by reaction of **3** and **9** respectively with ethyl oxalyl chloride in THF and triethylamine. Cyclization of **4** and **10** using Lawesson's reagent at room temperature gave excellent yields of the purified 1,3,4-thiadiazole-2-carboxylate esters **5** and **11**, respectively. Saponification of **5** and **11** gave sodium salts **6** and **12**, respectively. These sodium salts are unstable when exposed to high vacuum for extended periods of time and readily decarboxylate once all traces of water have been removed by the drying process. Conversion of **6** and **12** to the acid chlorides followed by *in situ* esterification gave the target materials **7** and **13**, respectively. Optimization of the esterification step is currently being undertaken in our laboratory.

3. Physical properties

The transition temperatures of the two final products **7** and **13** are as follows:

7 Transitions (°C) Cr 67.3 SmC_A* 82.5 SmC* 115.9 SmA* 142.4 Iso. Liq.
13 Transitions (°C): Cr 74.8 SmC* 126.9 N* 127.4 Iso. Liq.

Full experimental details and physical studies will shortly be reported in the journal *Liquid Crystals*.

4. Experimental

4.1. *(S)-1-Methylheptyl 4-[5-(4-octyloxphenyl)-1,3,4-thiadiazol-2-ylcarbonyloxy]benzoate (7)*

6 (0.98 g, 2.7 mmol) was suspended in anhydrous THF (20 mL) and anhydrous DMF (1 drop). The suspension was stirred vigorously and oxalyl chloride (0.2 mL, d 1.222 g/mL, 1.8 mmol) was added dropwise over 1 min. at room temperature. Once the evolution of gas had ceased, (*S*)-1-methylheptyl 4-hydroxybenzoate (0.69 g, 2.8 mmol) was added and the reaction was stirred vigorously. Anhydrous triethylamine (0.4 mL, d 0.726 g/mL, 3 mmol) was then added dropwise over 10 min. After 4 h. the triethylamine hydrochloride was filtered off and the resulting solution was stirred with an excess of ethanol (20 mL). The solvent was removed in vacuo and the crude product was purified by column chromatography [silica gel: ethyl acetate / petroleum ether, 1:9] to afford a yellow powder, which was crystallized from petroleum ether and dried in a desiccator. A white powder was obtained. Yield 0.29 g (28%). Transitions (°C) Cr 67.3 SmC_A* 82.5 SmC* 115.9 SmA* 142.4 Iso. Liq. (Rec. 15°C). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=6.0Hz), 1.20–1.43 (m, 18H), 1.35 (d, 3H, J=6.3Hz), 1.43–1.77 (m, 2H), 1.83 (quint, 2H, J=7.5Hz), 4.04 (t, 2H, J=6.6Hz), 5.16 (sext, 1H, J=6.0Hz), 7.01 (d, 2H, J=9.0Hz), 7.38 (d, 2H, J=9.0Hz), 8.00 (d, 2H, J=9.0Hz), 8.15 (d, 2H, J=9.0Hz). ^{13}C NMR ($CDCl_3$) δ 173.59, 165.37, 162.82, 157.64, 157.20, 153.57, 131.50, 130.37, 129.57, 121.51, 121.50, 115.48, 72.33, 68.59, 36.20, 31.96, 31.90, 29.48, 29.38, 29.32, 29.23, 26.14, 25.57, 22.82, 22.76, 20.24, 14.24, 14.23. Anal. Calcd for

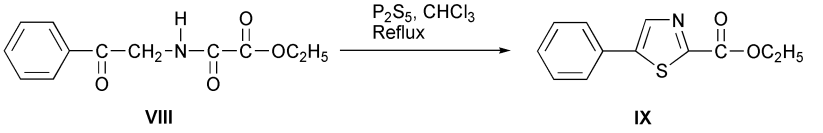
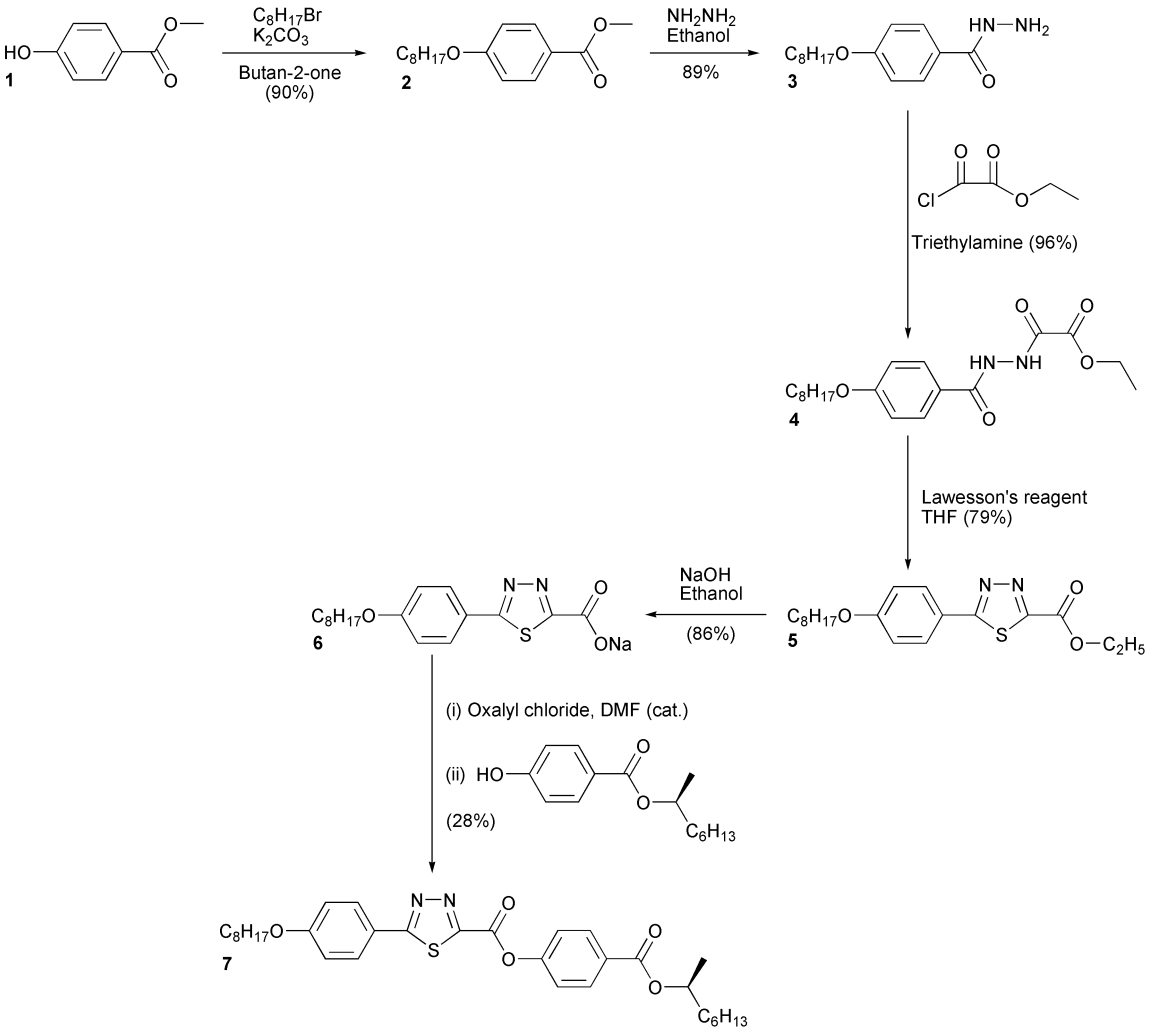


Figure 3. Tanaka's synthesis of ethyl 5-phenyl-2-thiazolecarboxylate.

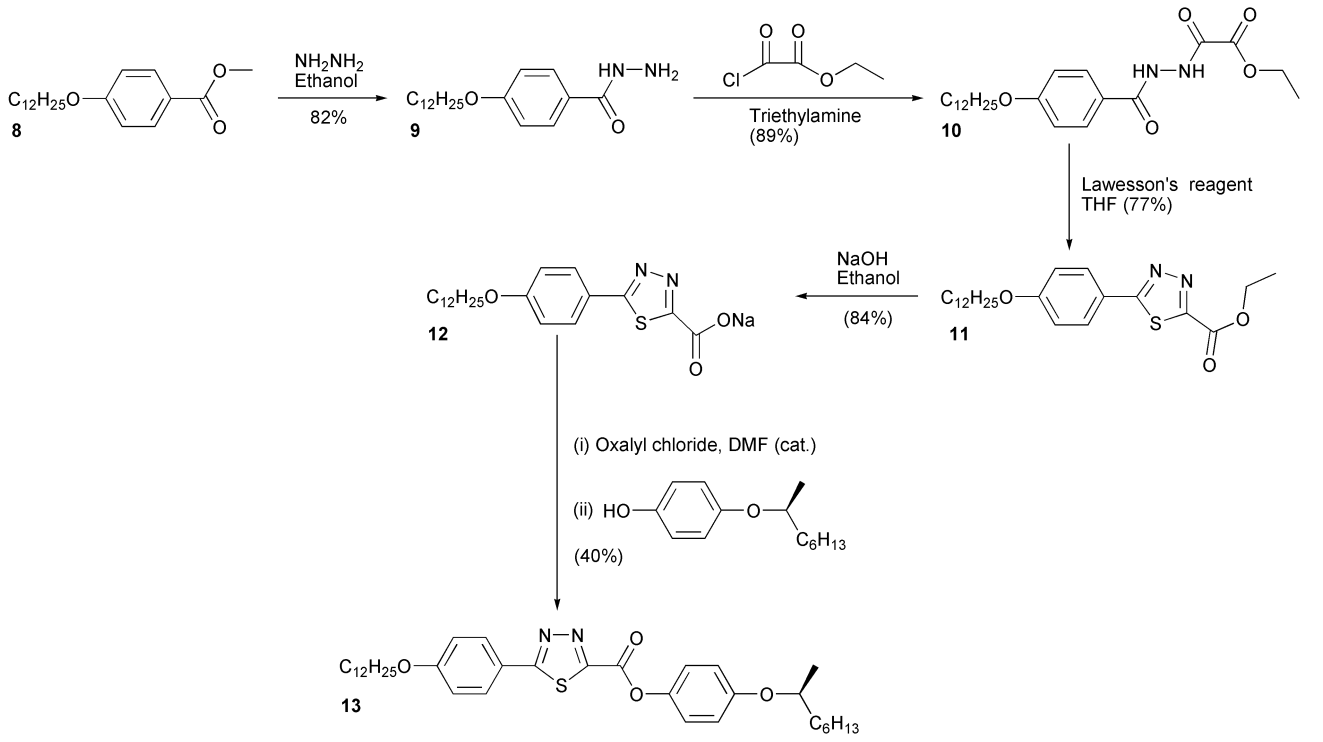


Scheme 1. Synthesis of (*S*)-1-methylheptyl 4-[5-(4-octyloxyphenyl)-1,3,4-thiadiazol-2-ylcarbonyloxy]benzoate.

$C_{32}H_{42}N_2O_5S$: C, 67.82; H, 7.47; N, 4.94; S, 5.66. Found: C, 67.36; H, 7.27; N, 5.12; S, 5.55.

4.2. *(S)-4-(1-Methylheptyloxy)phenyl 5-(4-dodecyloxyphenyl)-1,3,4-thiadiazol-2-ylcarboxylate (13)*

12 (0.89 g, 2.2 mmol) was suspended in anhydrous THF (20 mL) and anhydrous DMF (1 drop). The suspension was stirred vigorously and oxalyl chloride (0.2 mL, d 1.455 g/mL, 2 mmol) was added dropwise over 1 min. at room temperature. Once the evolution of gas had ceased, (*S*)-4-(l-methylheptyloxyl)phenol (0.46 g, 2.1 mmol) was added and stirred vigorously. Anhydrous triethylamine (0.3 mL, d 0.726 g/mL, 2 mmol) was then added dropwise over 10 min. After 4 h. the triethylamine hydrochloride was filtered off and the resulting solution was stirred with an excess of ethanol (20 mL). The solvent was removed in vacuo and the crude product was purified by column chromatography [silica gel: ethyl acetate / petroleum ether, 1:9] to afford a yellow powder which was crystallized from petroleum ether and dried in a desiccator. A white powder was obtained. Yield 0.48 g (40%). Transitions (°C): Cr 74.8 SmC* 126.9 N* 127.4 Iso. Liq. (Rec. 58.7°C). ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 6H, J=6.0Hz), 1.08–1.61 (m, 32H), 1.31 (d, 3H, J=6.0Hz), 1.80 (quint, 2H, J=6.9Hz), 4.02 (t, 2H, J=6.6Hz), 4.33 (sext, 1H, J=6.0Hz), 6.92 (d, 2H, J=9.0Hz), 6.99 (d, 2H, J=9.0Hz), 7.19 (d, 2H, J=9.0Hz), 7.97 (d, 2H, J=9.0Hz). ^{13}C NMR ($CDCl_3$) δ 173.21, 162.68, 158.82, 158.02, 156.69, 143.52, 130.29, 122.26, 121.76, 116.65, 115.42, 74.65, 68.55, 36.61, 32.08, 31.96, 29.80, 29.51, 29.43, 29.24, 26.12, 25.68, 22.85, 22.76, 19.85, 14.25. Anal. Calcd for $C_{35}H_{50}N_2O_4S$: C, 70.67; H, 8.47; N, 4.71; S, 5.39. Found: C, 70.49; H, 8.64; N, 4.87; S, 5.61.



Scheme 2. Synthesis of (*S*)-4-(1-methylheptyloxy)phenyl 5-(4-dodecyloxyphenyl)-1,3,4-thiadiazol-2-ylcarboxylate.

References

[1] S-I. Sugita, S. Toda, T. Teraji, A. Murayama, M. Ishikawa. *Mol. Cryst. Liq. Cryst.*, **226**, 7–12 (1993).

[2] S.-I. Sugita, S. Toda, T. Teraji. *Mol. Cryst. Liq. Cryst.*, **237**, 33–38 (1993).

[3] R. Lunkwitz, C. Tschierske, A. Langhoff, F. Gießelmann, P. Zugenmaier. *J. Mater. Chem.*, **7**, 1713–1721 (1997).

[4] W. Schafer, U. Rosenfeld, H. Zaschke, H. Stettin, H. Kresse. *J. Prakt. Chem.*, **331**, 631–636 (1989).

[5] K. Zab, D. Joachimi, E. Novotna, S. Diele, C. Tschierske. *Liq. Cryst.*, **18**, 631–637 (1995).

[6] M. Parra, J. Belmar, H. Zunza, C. Zuniga, S. Villouta, R. Martinez. *Bol. Soc. Chil. Quim.*, **38**, 325–330 (1993).

[7] M. Parra, J. Belmar, S. Villouta, R. Martinez, C. Zuniga, H. Zunza. *Bol. Soc. Chil. Quim.*, **40**, 175–182 (1995).

[8] M. Parra, J. Belmar, H. Zunza, C. Zuniga, S. Villouta, R. Martinez. *J. Prakt. Chem.*, **337**, 325–327 (1995).

[9] M. Parra, G. Fuentes, V. Vera, S.H. Villouta, S. Hernandez. *Bol. Soc. Chil. Quim.*, **40**, 455–460 (1995).

[10] M. Parra, S. Villouta, V. Vera, J. Belmar, C. Zúñiga, H. Zunza. *Z. Naturforsch., B: Chem. Sci.*, **52**, 1533–1538 (1997).

[11] M. Jesberger, T.P. Davis, L. Barner. *Synthesis*, 1929–1958 (2003).

[12] J.W. Goodby. *Mol. Cryst. Liq. Cryst.*, **292**, 245–263 (1997).

[13] J.W. Goodby. Properties and structures of ferroelectric liquid crystals. In *Ferroelectric liquid crystals*, G.W. Taylor (Ed.), Gordon and Breach, Philadelphia, pp. 99–248 (1991).

[14] C. Tanaka, K. Nasu, N. Yamamoto, M. Shibata. *Chem. Pharm. Bull.*, **30**, 4195–4198 (1982).

[15] H.H. Freedman, R.A. Dubois. *Tetrahedron Lett.*, 3251–3254 (1975).

[16] S.R. Sandler, W. Karo. Hydrazine derivatives, hydrazones, and hydrazides. In *Organic functional group preparations*, H.H. Wasserman (Ed.), Academic Press, New York, pp. 434–465 (1983).