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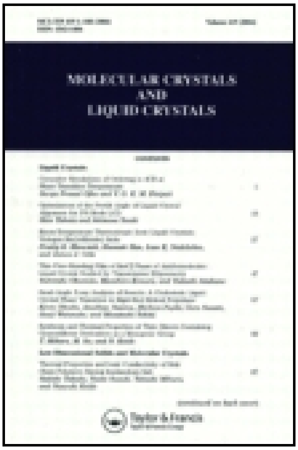

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A Convenient Synthesis of 4-Alkyl and 4-Cyano Thiophenols

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A Convenient Synthesis of 4-Alkyl and 4-Cyano Thiophenols

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INTRODUCTION

Substituted phenyl thiobenzoates[1] represent a new a quite interesting class of liquid crystals which are reported to have wider nematic ranges and higher dielectric anistropies than their corresponding phenyl benzoate analogs. At present, however, very few substituted thiophenols are commercially available and laboratory synthetic routes to many such compounds can be difficult. This is especially the case with 4-cyanothiophenol, whose synthesis has been accomplished by reaction of 4-cyanobenzene diazonium ion with potassium ethyl xanthate and hydrolysis of the resulting ester.[1c] For the syntheses of 4-cyano and 4-butylthiophenol, we report here an application of the method of Newman and Karnes.[2]

RESULTS AND DISCUSSION

O-Phenyl dimethylthiocarbamates, heated in a nitrogen atmosphere to 200–280°C, are transformed to their S-phenyl isomers whose subsequent saponification yields the desired thiophenols (Figure 1).

Tentative results indicate that the 1,3 isomerization is eased by electron withdrawing substitutents in the para position, which corresponds precisely to those thiophenols which are difficult to obtain by the more usual method[3] of reduction of the sulfonyl chloride. The conversion of 4-cyanophenol to 4-cyanothiophenol proved especially facile, proceeding in an overall yield of 55%. On the other hand, while this brief report represents no real effort at

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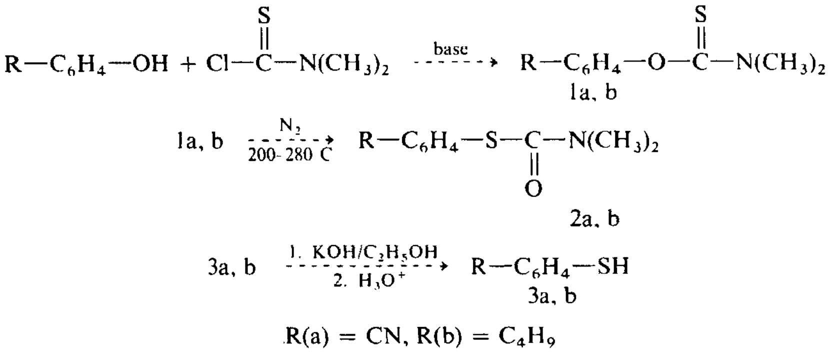

$$R{-}C_6H_4{-}OH + Cl{-}\overset{\overset{S}{\|}}{C}{-}N(CH_3)_2 \xrightarrow{\text{base}} R{-}C_6H_4{-}O{-}\overset{\overset{S}{\|}}{C}{-}N(CH_3)_2 \quad \text{1a, b}$$

$$\text{1a, b} \xrightarrow[200\text{–}280\,°C]{N_2} R{-}C_6H_4{-}S{-}\underset{\underset{O}{\|}}{C}{-}N(CH_3)_2 \quad \text{2a, b}$$

$$\text{3a, b} \xrightarrow[2.\ H_3O^+]{1.\ KOH/C_2H_5OH} R{-}C_6H_4{-}SH \quad \text{3a, b}$$

$R(a) = CN$, $R(b) = C_4H_9$

FIGURE 1

obtaining optimum yields, the conversion of 4-butylphenol to its thio analog, in an overall yield of 42%, appeared to offer no real large scale preparative advantage over the reduction of alkylbenzene sulfonylchlorides.[3b]

During the thermal isomerization step, care must be taken to maintain a thorough nitrogen purge of the reaction flask. Formation of disulfides at this point may be further minimized by including a quantity of 20 mesh zinc granules in the reaction flask.[4]

EXPERIMENTAL

Mass spectra were obtained with a Hewlett-Packard 5982 Dual-Source mass spectrometer. Infrared spectra were generated by a Pye Unicam SP1000 instrument. Melting points were uncorrected.

1) O-(4-cyanophenyl)-N,N-dimethylthiocarbamate (1a). 4-Cyanophenol (30.0g, 0.252 m) was dissolved in 500 mls of dry acetone with 32 g (0.252 m) *N*,*N*-dimethylthiocarbamoylchloride. The reagents were mechanically stirred under reflux with 40.0 g (0.29 m) of anhydrous potassium carbonate for three hours. Isolation and recrystallization of the product from benzene/hexane returned 34.0 g (65%) of la. The m.p. was 116–7°C, purity by g.l.c. 99.7%. The mass spectrum showed m/e (intensities) of 206 (20%), 134 (10%), 88 (100%), 72 (100%). Strong, characteristic i.r. bands were observed at 1550, 1595 cm^{-1}.

2) S-(4-cyanophenyl)-*N*,*N*-dimethylthiocarbamate (2a). Compound la (24 g, 0.063 m) and 4.0 g of 20 mesh zinc granules were heated two hours at 210–220°C under dry nitrogen. Recrystallization of the product from CCl_4-hexane gave 23.0 g (96%) of 2a, m.p. 102–3°C. The mass-spectrum showed

m/e (intensities) of 206 (2%), 134 (10%), 107 (7%), 90 (20%), 72 (100%). The carbonyl i.r. band was at 1665 cm^{-1}.

3) 4-Cyanothiophenol (3a). Compound 2a (23.0 g, 0.060 m) was refluxed with 10.0 g (0.178 m) KOH in 250 mls abs ethanol for two hours. The cooled reaction mixture was acidified to give 14.5 g (92%) of 3a, 99.8% purity by g.l.c. The m.p. was 50–51°C. The mass spectrum showed the anticipated molecular ion at m/e 135.

4) O-(4-butylphenyl)-*N*,*N*-dimethylthiocarbamate (1b). 4-Butylphenol (44.0 g, 0.29 moles) was dissolved in 200 mls of methanol with 16.5 g (0.29 m) of KOH and the solution chilled to 0°C. *N*,*N*-Dimethylthiocarbamoyl chloride (36.2 g, 0.284 m) was added as a solid and the reaction mixture stirred overnight. Upon work-up, the reaction mixture gave a dark oil, which, distilled at 170°C (10^{-4} Torr) yielded 44.0 g (65%) of a liquid with spectral characteristics consistent with lb: m/e (intensities) = 237 (50), 180 (10), 161 (5), 107 (10), 88 (100); strong, characteristic i.r. absorption at 1530, 1500 cm^{-1}.

5) S-(4-butylphenyl)-*N*,*N*-dimethylthiocarbamate (2b). Compound lb was pyrolysed for three hours at 280°C, as previously described. Distillation of the product at 10^{-4} Torr gave a crystalline fraction of b.p. 150–65°C, which, recrystallized from pentane at −20°C gave 30 g (68%) of 2b, g.l.c. purity 99.7%. The mp. was 44–5°C; spectral characteristics were m/e (intensities) 237 (100%), 165 (14%), 137 (10%), 123, 121, 109 (20% each) and carbonyl i.r. absorption at 1655 cm^{-1}.

6) 4-Butylthiophenol (3b). Compound 2b (19.0 g, 0.080 m) was refluxed 5 hours in 100 mls ethanol with 11.0 g (0.196 m) of KOH. The thiol was isolated from the acidified filtrate and distilled at 140°C (10^{-4} Torr) to give 12.7 g (95%) of 3b. The mass spectrum showed the anticipated molecular ion at m/e = 166.

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