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Syntheses of Liquid Crystal Intermediates 4-Alkylbenzenethiols and Phenols†

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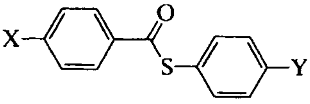
An improved synthesis of 4-alkylbenzenethiols has been developed. Sulfonation of alkylbenzenes in sulfuric acid at 75° yields 4-alkylbenzene sulfonic acid salts which are free of other positional isomers in high yields. Conversion to the thiols via the sulfonyl chlorides provide a high yield, 3 step synthesis of pure 4-alkylbenzenethiols. Fusion of the salts with potassium hydroxide provides a simple synthetic approach to pure 4-alkylphenols as well. Both the thiols and phenols are useful intermediates in the preparation of mesomorphic compounds.

INTRODUCTION

The increased stability of 4,4′-disubstituted benzenethiobenzoates, **1**



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over that found in the Schiff bases, azo- and azoxybenzenes and stilbenes has stimulated interest in investigating the mesomorphic properties of these compounds.[1–3] Since we wanted to prepare large quantities of several of these

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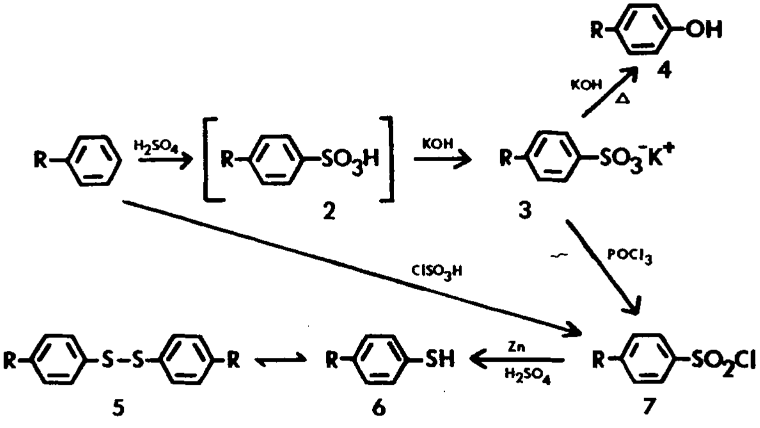


SCHEME 1

thioesters for phase transition studies[4,5] as well as possibly some deuterated analogs (such as with $X = C_nD_{2n+1}O$ or $Y = C_nD_{2n+1}$), a much more efficient route for preparing pure 4-alkylbenzenthiols **6** (scheme 1) than those previously used[1–3] was needed.

Seemingly, the easiest approach for preparing these thiols would involve sulfonation of alkylbenzenes using either sulfuric or chlorsulfonic acid followed by reduction of the sulfonyl chloride (scheme 1). However, such sulfonations are known to produce mixtures of isomers.[6–8] For example, sulfonation of toluene in concentrated sulfuric acid at 75° forms a mixture consisting of *ca.* 75% 4-, 19% 2- and 6% 3-isomers of toluenesulfonic acid.[9] This likelihood of obtaining a mixture of isomers which could be more difficult to separate with longer alkyl groups present has apparently discouraged much use of this method for preparing the thiols. Chlorosulfonation has been used[2,3] and yields of 70–80% reported[2] but nmr data was not provided to determine the isomeric content of the product.

The more difficult approach of preparing these thiols through the hydrolysis of the corresponding xanthates has been used more extensively.[1] This method has several major disadvantages. It is a low yield, many step procedure which yields material that is difficult to purify. 4-Alkylanilines, which are needed as the starting material, are either not commercially available or are very expensive and they are not easily prepared in high yields.[10] The use of large excesses of alkyl acid chlorides in the preparation of these anilines makes this synthetic approach much too expensive for preparing chain deuterated thiols. Although the thioesters can be readily purified if impure thiol is used, in the case where $X = C_nD_{2n-1}O$, it is more desirable to purify the thiol to avoid losses of expensive deuterated material. Our experience with this method indicates that obtaining pure thiol is very difficult. An attempt to purify the intermediate xanthate by distillation gave instead the thiol **6** via the Chugaev rearrangement. This could also serve as a method for preparing the thiol but again the material isolated was difficult to purify.

Sulfonation of alkylbenzenes to obtain the thiols (scheme 1) offers the advantage that the alkylbenzenes are commercially available. We felt that this method had not been investigated thoroughly enough to ignore as a better route to the thiols. Our hope was to develop conditions which would maximize the amount of the 4-isomer fomed and that this could be separated easily from other isomers. Once this could be achieved conversion to the thiol seemed to be straight forward.

RESULTS AND DISCUSSION

The effect of various conditions and reagents on yields and product formation in the sulfonation of aromatic systems has been extensively reviewed.[6,7,11–13] Although sulfonations of alkylbenzenes of various chain lengths have been reported, often isomeric determinations were not performed or the isomers separated.[14,15] NMR spectroscopy has not been used to determine isomeric content.

Seemingly, chlorosulfonic acid would be the reagent of choice for preparing the thiol since this would yield the sulfonyl chloride **7** directly. Yields of the 4-isomer in which $R = n\text{-}C_2 - C_6$ of 67–86% have been reported when a sulfonation temperature of 5–10° was used.[16] Yet a detailed procedure for the preparation of 4-toluenesulfonyl chloride gives a yield of only 22% of the 4-isomer.[17] Our attempt at chlorosulfonation at 5° gave a mixture of the 2- and 4-isomers ($R = C_5H_{11}$) with the 2-isomer predominating and separation being difficult. At 75°, the 4-isomer was isolated in yields of 16–20% and the remaining material decomposed to a black tar during the distillation. An nmr spectrum (Figure 1) of the crude material before distillation showed a complex aromatic proton pattern suggesting the presence of other positional isomers and probably disulfonated compounds.

Sulfonation of alkylbenzenes (C_8–C_{12}) with sulfuric acid at 55° reportedly gives a mixture of about 80% of the 4- and 20% of the 2-isomers (determined by derivatization)[8,18] which is comparable to that obtained for toluene.[9] We found that the 4-isomer could be isolated free of other isomers in yields usually $>80\%$ when sulfonation was done at 75° using concentrated sulfuric acid. Obtaining complete sulfonation or avoiding polymerization seemed to be more of a problem than positional isomer contamination.

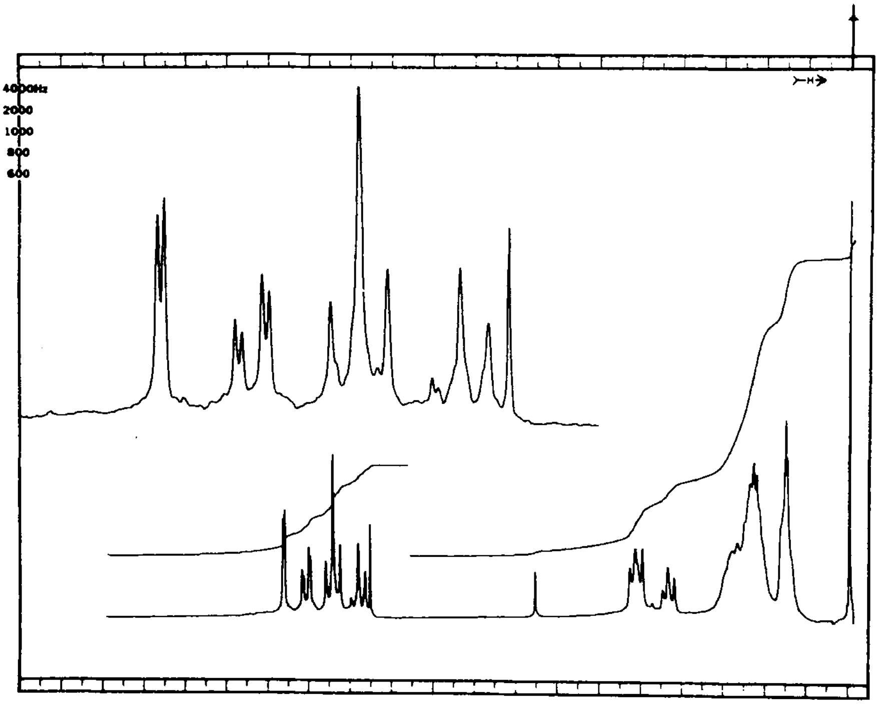


FIGURE 1 NMR spectrum for crude product from chlorosulfonation of *n*-pentylbenzene at 75°.

The temperature at which complete sulfonation occurred depended on the alkyl chain length as shown by the data presented in Table I. This is not surprising in view of kinetic studies which showed the following order of reactivity.[19,20]

$$R = \text{Me} > \text{Et} > i\text{-Pr} > t\text{-Bu}$$

We found that at 75°, essentially complete sulfonation could be obtained for all the straight chain alkylbenzenes studied ($R = C_5$–C_{12}); yields varied from 71–89% for both large and small scale reactions.

In all cases, it was easier to isolate and purify the sulfonic acids as either the potassium or sodium salts. However, because of the different solubilities of these salts in water depending on the alkyl chain length (decreases with increasing chain length), it was necessary to develop two different isolation procedures. Details for both procedures are given in the experimental section.

Conversion of the sulfonate salts **3** to the sulfonyl chlorides **7** was achieved using either phosphorous pentachloride or phosphoryl chloride (see Ref. 21). Phosphoryl chloride became the reagent of choice since higher yields were

TABLE I

The effect of temperature on the sulfonation of alkylbenzenes

R	Temperature °C	Time (min)	% Yield of 3	% Recovered Alkylbenzene
C_5H_{11}	27 (RT)	60	72	23
C_5H_{11}	50	30	87	7
C_8H_{17}	50	60	80	19
$C_{10}H_{21}$	50	40	3	91
$C_{10}H_{21}$	75	60	82	~1
$C_{12}H_{25}$	75	60	85.4	—

obtained and foaming during the reaction was considerably less. Data for the sulfonyl chlorides are presented in Table II.

Reduction of the sulfonyl chlorides to the thiols **6** in yields of 68–80% (see Table III) was achieved using zinc and sulfuric acid.[22] Failure to wash the ether extract containing the thiol thoroughly with water during work-up decreased the yields significantly. Apparently, acid contaminants remaining in the crude material caused the thiol to oxidize more readily to the disulfide. The disulfide, which remained after distilling the thiol, could not be distilled; further heating caused it to decompose to the thiol. However, this also gave large amounts of non-distillable tars decreasing the total yield of the thiol. Attempts to reduce either this disulfide **5** or the sulfonyl chloride **7** to the thiol **6** ($R = C_5H_{11}$) using lithium aluminum hydride by known methods[23,24] were unsuccessful. Preparatory thin layer chromatography of the thiol produced the disulfide confirming the case of oxidation. Consequently, all purified thiol samples were stored in sealed ampules.

In order to be certain that our sulfonic acid salts were the 4-isomers and free of small amounts of other isomers, all compounds in this work were studied extensively by NMR spectroscopy. Spectra of the salts in D_2O showed

TABLE II

Synthesis of 4-Alkylbenzenesulfonyl Chlorides Using $POCl_3$

R	% Yield	bp (°C/torr)
C_5	60,86[a]	134/0.30[b]
C_6	81	167/1.4
C_8	72	166/0.45
C_{10}	76	182/0.55
C_{12}	61	205 (0.20)

[a] Obtained using PCl_5

[b] mp = 45–46, lit. value 43° (ref. 16).

TABLE III

4-Alkylbenzenethiols

R	% Yield	bp (°C/torr)
C_5	68	89-93/0.66
C_6	80	119/1.0
C_8	51	159/3.5
C_{10}	76	162/167/2.4
C_{12}	74	154/159/0.7

a symmetrical aromatic proton pattern which is strong evidence for the 4- rather than the 2- or 3-isomers (Figure 2a). Expansion of this region (Figure 2b) provided confirmation that even small amounts of the other isomers were not present. This was true of both first and second crop materials; third crops, isolated in small amounts, usually showed a less symmetrical pattern suggesting that the other isomers could be in the mother liquors. We found similar results with toluene indicating that the isomeric ratio does not depend significantly on alkyl chain length. Since we did not have authentic samples of the 2- and 3-isomers of the sulfonic acid to use for comparison but did have the 2-isomer of the sulfonyl chloride (from sulfonation with chlorosulfonic acid), we compared the nmr spectra for the 2- and 4-*n*-pentylsulfonyl chlorides (Figures 3 and 4 respectively). Although the aromatic proton pattern is asymmetrical and more complex for the 2- than for the 4-isomer, there is enough similarity to make it difficult to eliminate the possibility that small amounts of the 2-isomer are present in the 4-isomer. Sadtler reference curves for 2- (no. 6933) and 4- (no. 9393) toluenesulfonyl chloride showed the same aromatic proton patterns for the corresponding isomers. However, the region at 2.5–3.2δ for the α-methylene protons in the longer chain compound provides additional support that the 4-isomer is free of the 2-isomer. The spectrum of the 4-isomer shows one well-defined triplet centered at 2.75δ whereas a pair of triplets centered at 2.75 and 3.15δ occurs in the spectrum for the 2-isomer. This indicates that in the 2-isomer the methylene protons are not equivalent; one has its chemical shift influenced only by the aromatic ring whereas the other is shifted further downfield by the influence of the 2-sulfur substituent. This can only be explained by hindered rotation of the alkyl chain about the alkyl-aromatic C—C bond.

A good indication that nmr spectra provide an adequate method for detecting small amounts of the 2-isomer is shown by the spectrum for the *n*-pentylbenzenesulfonyl chloride obtained by chlorosulfonation at 75° (Figure 5). Although the aromatic proton pattern indicates the presence of primarily the 4-isomer, it is not as clean as that observed in Figure 4. The α-methylene proton region confirms the presence of another isomer by the presence of a weak second triplet at 3.15δ.

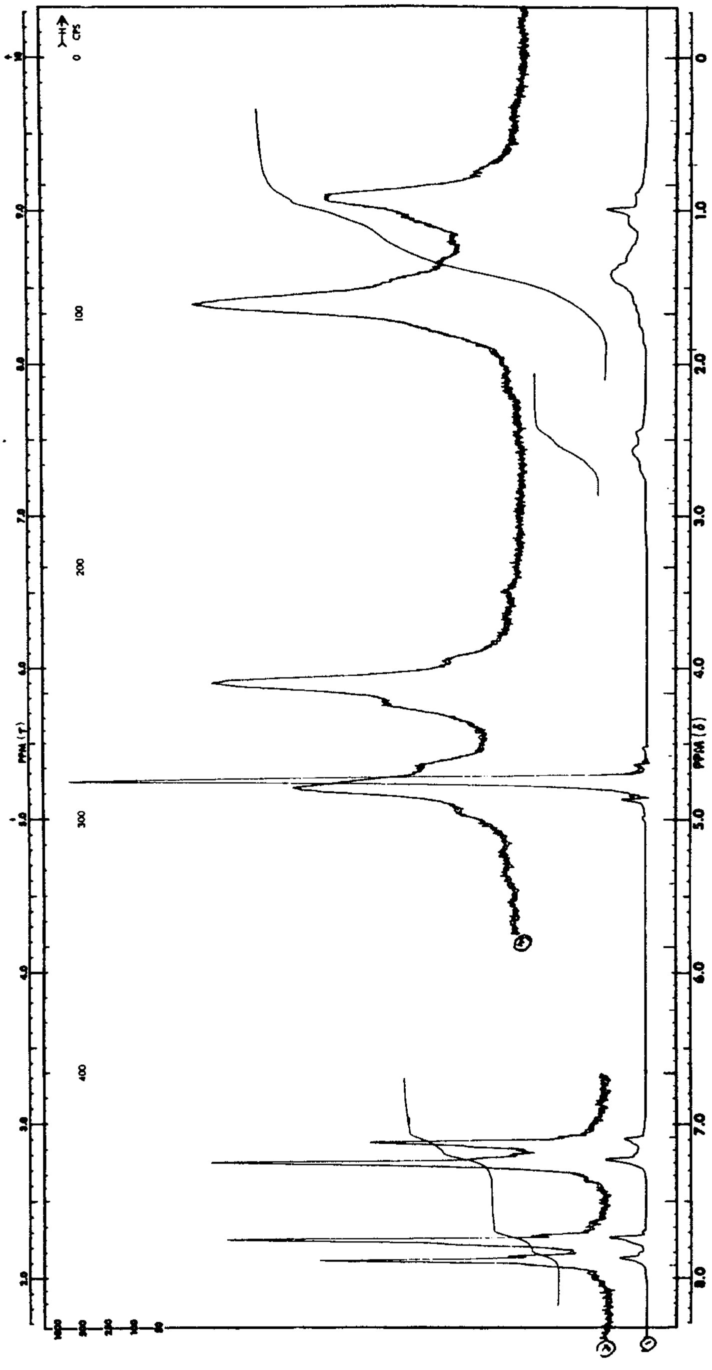


FIGURE 2 NMR spectrum for potassium 4-*n*-pentylbenzenesulfonate.

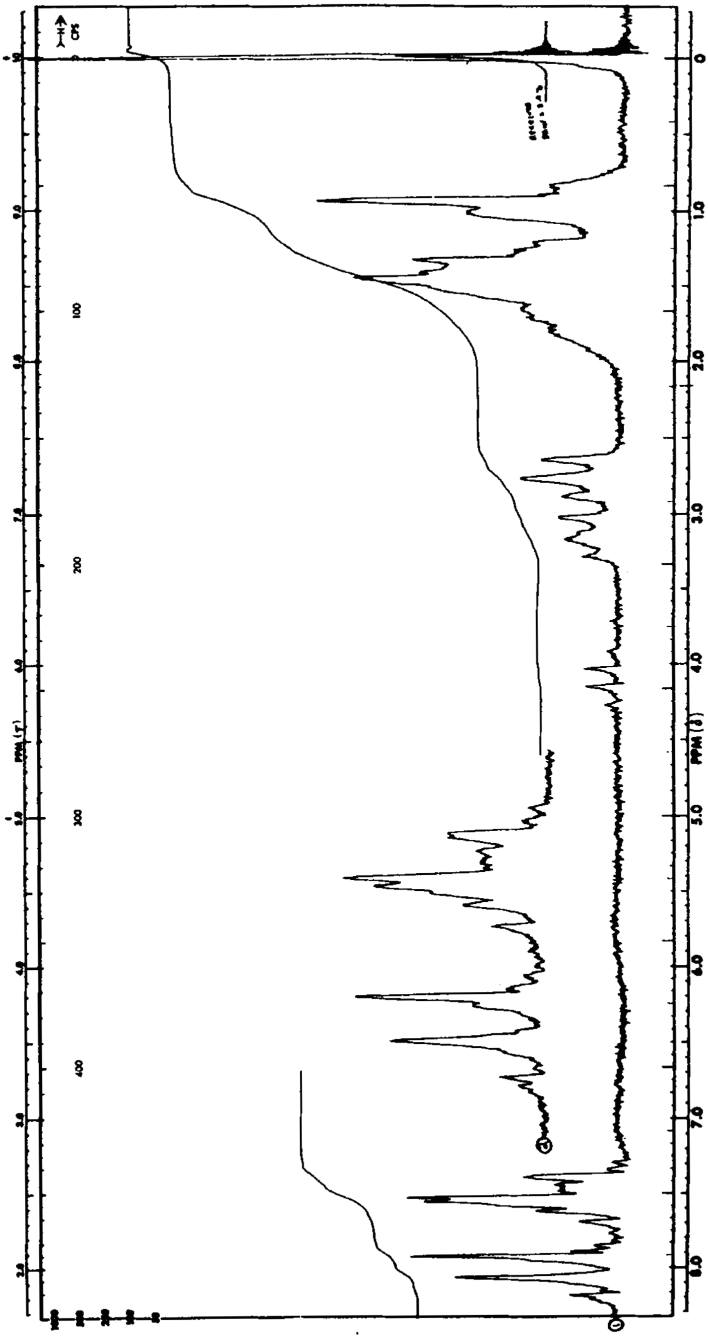


FIGURE 3 NMR spectrum for 2-*n*-pentylbenzenesulfonyl chloride.

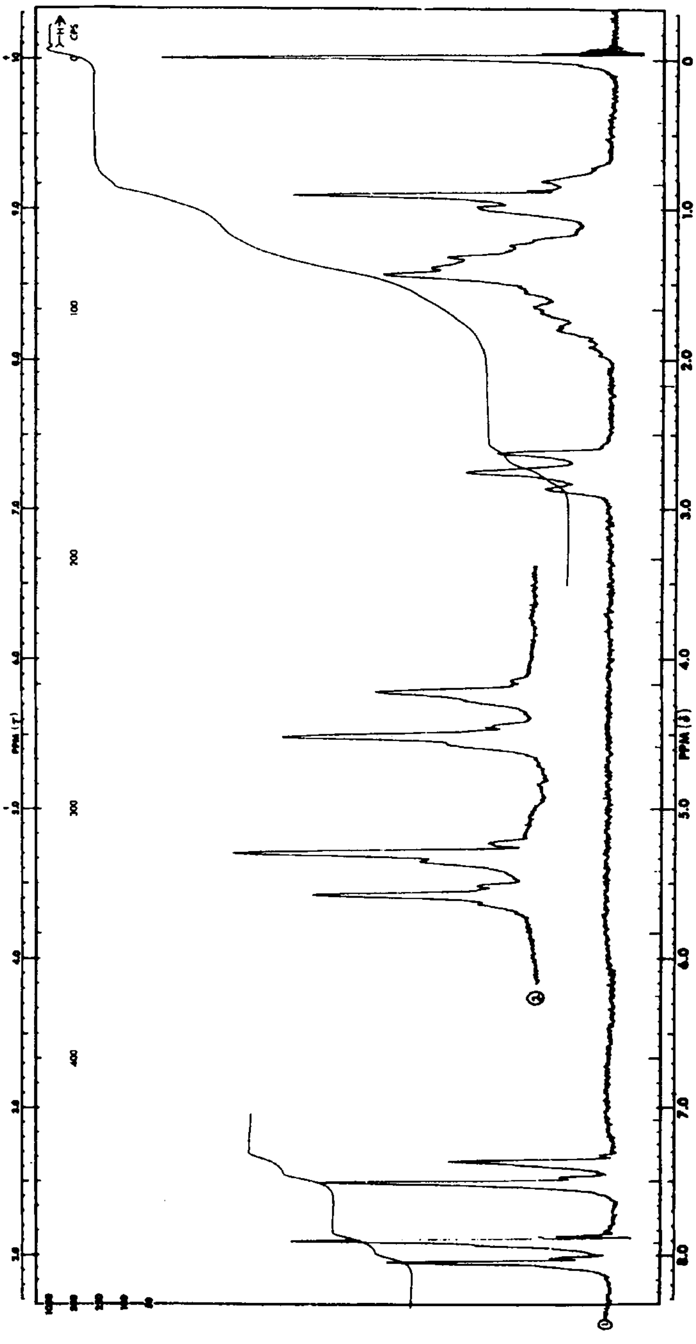


FIGURE 4 NMR spectrum for 4-*n*-pentylbenzenesulfonyl chloride.

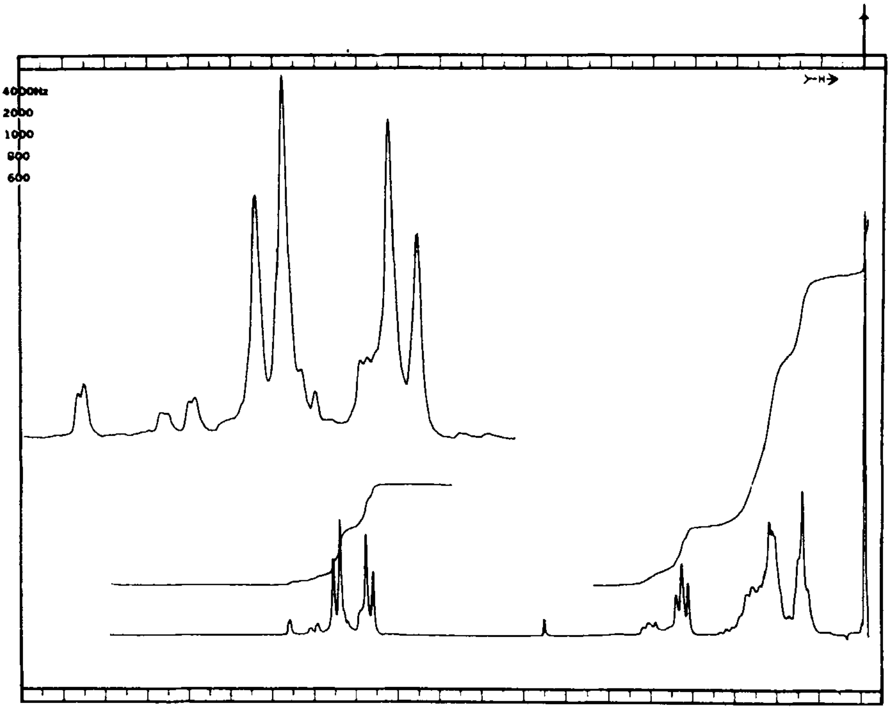


FIGURE 5 NMR spectrum for 4-*n*-pentylbenzenesulfonyl chloride from chlorosulfonation of n-pentylbenzene at 75°.

The aromatic proton region for the thiol (Figure 6) again shows a symmetrical pattern but with the doublets having a much smaller difference between their chemical shifts. Again there is no additional triplet for the α-methylene protons but we cannot be sure that this is also not true for the 2-isomer since the SH group is much smaller than the SO_2Cl group. The nmr spectrum for the material believed to be the disulfide is essentially the same as that for the thiol except for the absence of the SH peak at 3.12δ. This proved to be one of the few methods for distinguishing the disulfide from the thiol.

Not only does sulfonation of alkylbenzenes with sulfuric acid provide a good synthesis for 4-alkylbenzene thiols but by making 4-alkylbenzene sulfonic acids readily available, it is useful as a synthetic approach to 4-alkylphenols, **4** (scheme I). Fusion of the salts **3** ($R = C_8$–C_{10}) with sodium hydroxide in an iron pot[25] gave yields of 48–63%. Although other methods are available for preparing these phenols,[26,27] this approach is simple and provides material free of the 2-isomer in good yields.

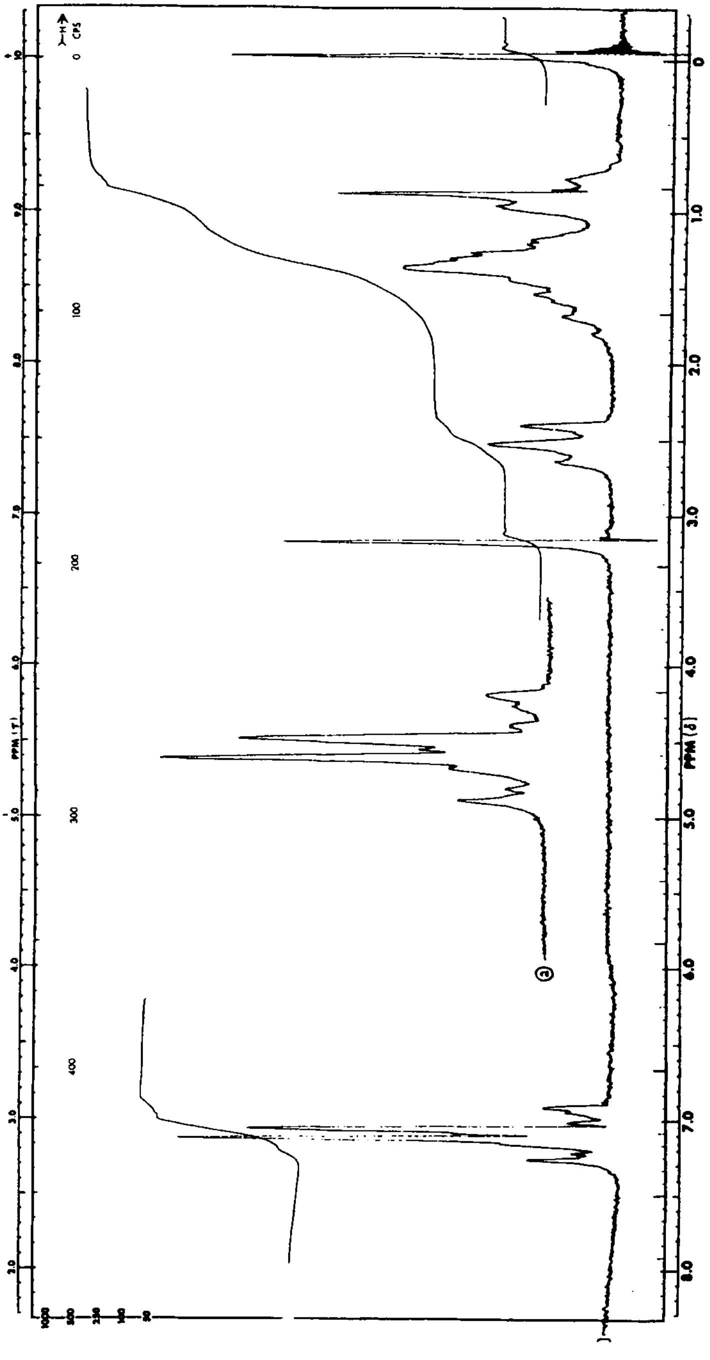


FIGURE 6 NMR spectrum for 4-*n*-pentylbenzene thiol.

CONCLUSIONS

Sulfonation of alkylbenzenes in sulfuric acid at 75° yields 4-alkylbenzenesulfonic acid salts which are free of other isomers in high yields. Conversion to the thiols via the sulfonyl chlorides provides a high yield 3 step synthesis of pure 4-alkylbenzene thiols whereas fusion of the salts with potassium hydroxide provides a simple synthetic approach to pure 4-alkylphenols.

EXPERIMENTAL

Materials

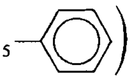
Alkylbenzenes were obtained from Aldrich Chemical Company and used without distillation unless colored. Distillation of colored materials was necessary to avoid polymerization/decomposition. Other commercially available chemicals and solvents were not purified before use. Organic extracts were dried over anhyd. Na_2SO_4 followed by Linde No. 4A molecular sieves.

EXPERIMENTAL TECHNIQUES

Melting points were determined in capillary tubes using a Hoover-Thomas instrument and are corrected. Tlc data were obtained using Anal-Tech Silica gel GF 2.5 × 10 cm Uniplates® (250 μ) with *UV* light as the detector. A Perkin-Elmer model 700 (ir), Varian A-60 or FT-80 (nmr, TMS as the standard in organic solvents) and Associated Electronics Industries Model MS-12 (mass spectra, 700 eV) instruments were used as analytical tools. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

Chlorosulfonation of *n*-Pentylbenzene

a. at 0–5° *n*-Pentylbenzene (14.8 g, 0.10 mole) was added dropwise in 20 min, with stirring to $ClSO_3H$ (36.8 g, 0.316 mole) at 0–5°. This reaction mixture was stirred at 0–5° for 4 hr, stored at this temperature for 17 hr and then poured onto *ca.* 200 g ice. The precipitate was collected by filtration, washed with cold H_2O (3 × 200 ml) and dried *in vacuo* for 17 hr to give 3.5 g (14.2%) of a white solid shown to be 4-*n*-pentylbenzenesulfonyl chloride, 7 ($R = C_5H_{11}$): mp 36–40°. Recrystallization from petroleum ether (30–60°) gave 3.2 g (13.0%) of material with mp 44–46°.

The aqueous filtrate was extracted with Et_2O (2 × 1*l*) and the Et_2O layer dried, filtered and the solvent removed (Rotovap) to give 14.5 g (57.7%) of a light brown liquid. Some of this (9.8 g) was distilled at 120° (0.35 mm) to give 5.1 g of 2-*n*-pentylbenzenesulfonyl chloride: tlc (CCl_4) R_f = 0.26 (major), 0.34 (minor) R_f 4-isomer = 0.26); ir (film) 1600 (Ar, medium) and 1380 and 1180 cm^{-1} (SO_2Cl, intense); nmr (CCl_4, Figure 3) δ8.10–7.00 (m, 4, ArH), 3.30–2.90 (2*t*, 2, *J* = 7.5 Hz, $ArCH_2$) and 2.0–0.60 (*m*, 9, C_4H_9) and mass spec m/e (rel intensity) 248 (5.95, $^{37}ClM^+$) 246 (17.38, $^{35}ClM^+$), 211 (38.52, $ArSO_2+$), 1.92 (6.86, $C_7H_8SO_2$ $^{37}Cl+$), 190 (13.29, $C_7H_8SO_2$ $^{35}Cl+$), 147 (17.20, C_5— ) and 91 (100, C_7H_7+).

b. at 75° To cooled (15°) $ClSO_3H$ (44.5 ml = 0.672 mole) was added dropwise *n*-pentylbenzene (20 g = 0.135 mole) at a rate slow enough to maintain a temperature of 15°. After completion of the addition, the reaction solution was heated at 55–60° for 2 hr, poured slowly with stirring onto ice and extracted with CCl_4. The CCl_4 was washed with H_2O, 5% qa Na_2CO_3 soln and H_2O, dried overnight, filtered and the solvent removed (Rotovap) to give a brown liquid (30.9 g). Distillation at 163° (6.4 mm) gave 6.50 g (19.5%) of a yellow liquid which crystallized on standing to a colorless solid shown to be primarily 4-*n*-pentylbenzenesulfonyl chloride by nmr (CCl_4, Figure 5).

Potassium 4-*n*-Pentylbenzenesulfonate, 3 (R = C_5H_{11}, general method for *R* = C_5, C_6

To 18.6 ml concd H_2SO_4 stirred in an Erlenmeyer flask heated in an oil bath at 74° was added *n*-pentylbenzene (10.0 g, 67.7 mmoles). This mixture, which turned a brownish color after the addition was completed, was stirred vigorously at this temperature for 1 hr. The cooled (*ca.* 10°) reaction soln was poured into cold H_2O (30 ml) and extracted with $CHCl_3$ (2 × 100 ml). The $CHCl_3$ layer was extracted with 200 ml H_2O and the aqueous layer made basic with a satd aq KOH soln. This was boiled down to *ca.* 75 ml, cooled to 5° and the resulting crystals collected and dried to give 14.5 g (80.5%) of the salt. A small amount was recrystallized from H_2O to give an analytical sample of compound **3** (*R* = C_5H_{11}): mp ~300°; tlc (CH_3CN) streaking spot at the origin (R_f for *n*-pentylbenzene = 0.88), (MeOH) R_f = 0.74 (R_f for 4-toluenesulfonic acid = 0.78); ir (nujol) 830, 810 (sulfonate, medium) and 750 cm^{-1} (sulfonate, weak) and nmr (D_2O), Figure 2) δ (from H_2O) −3.05 (d, 2, *J* = 8 Hz, ArH *ortho* to *S*), −2.43 (d, 2, *J* = 8 Hz, ArH ortho to alkyl), +2.16 (unresolved m, 2, $ArCH_2$) and 2.65–4.68 (m, 9, C_4H_9).

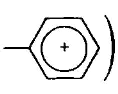
Anal. Calcd for $C_{11}H_{15}O_3KS$: C, 49.59; H, 5.68; S, 12.03. Found: C, 49.50; H, 5.67; S, 12.15.

Potassium 4-*n*-Dodecylbenzenesulfonate, 3 ($R = C_{12}H_{25}$) general method for $R = C_7$–C_{12}

A mixture of *n*-dodecylbenzene (15.0 g 61.0 mmoles) and 16.8 ml concd H_2SO_4 was stirred vigorously at 80–90° for 1 hr, cooled to RT and then gradually poured with stirring into *ca.* 300 ml 10% aq KOH soln. (pH was checked to be sure mixture was basic). The resulting white precipitate was collected by filtration over glass fiber filter paper, washed with 50 ml cold H_2O and dried to give 21.7 g (97.7%) of the crude salt. Recrystallization from 200 ml H_2O gave 18.1 g (81.5% of the salt **3** ($R = C_{12}H_{25}$).

4-*n*-Pentylbenzenesulfonyl Chloride, 7 ($R = C_5H_{11}$)

A mixture of the salt **3** ($R = C_5H_{11}$, 10 g, 38 mmoles) and PCl_5 (3.7 g, 18 mmoles) was hand stirred first at RT and then gradually heated in an oil bath to ~ 170°. Foaming occurred if the mixture was heated too rapidly but subsided once the fluid mixture became more solid. The solid became more fluid and yellow with additional heating which was continued for 1 hr. The hot mixture was poured into 250 ml cold H_2O and extracted with 2 × 150 ml $CHCl_3$. The $CHCl_3$ layer was dried, filtered and the solvent removed (Rotovap) to give 9.0 g (96%) of the crude product; mp 37–44°. Recrystallization from 90 ml ligroine (60–90°) with a Norit treatment gave 1.4 g (14.9%) of the sulfonyl chloride, 7 ($R = C_5H_{11}$): mp 45–46° (lit[16] mp 43°); tlc (CCl_4) $R_f = 0.26$ (R_f 4-toluenesulfonyl chloride = 0.14), (CH_3CN) $R_f = 0.88$ (starting material $R_f = 0$); ir ($CHCl_3$) 1590 (Ar, medium), 1370 and 1180 cm^{-1} (SO_2Cl, intense); nmr (CCl_4, Figure 4) δ7.81 (d, 2, $J = 8.5$ Hz, ArH *ortho* to SO_2Cl), 7.30 (d, 2, $J = 8.5$ Hz, ArH *ortho* to alkyl), 2.69 (*t*, 2, $J = 7.5$ Hz, $ArCH_2$) and 2.00 – 0.60 (m, 9, C_4H_9); and mass spectrum m/e (rel intensity) 248 (10.66, $^{37}ClM^+$), 246 (29.71, $^{35}ClM^+$), 211 (67.38, $ArSO_2+$), 192 (14.53, $C_7H_8SO_2$ $^{37}Cl^+$), 190 (39.29, $C_7H_8SO_2$ $^{35}Cl^+$), 147 (34.02,

C_5H_{11} ) and 91 (100, C_7H_7+).

A second crop (2.1 g = 22.4%) with mp 42.5–44° was obtained from the filtrate. Recrystallization of the product from a large scale reaction (251 g in 300 ml) from CCl_4 gave a 60% yield of the product. However, distillation at 134° (0.3 mm) gave a higher yield of 85.8%.

4-*n*-Decylbenzenesulfonyl Chloride, 7 ($R = C_{10}H_{21}$)

A mixture of the salt, 3 ($R = C_{10}H_{21}$, 10 g, 35.7 mmoles) and $POCl_3$ (4.30 g, 28.1 mmoles) was treated in the same manner as was used to prepare the C_5

homolog. The reaction mixture was added to ~20 ml cold H_2O and extracted with $CHCl_3$. The dried organic layer was filtered and the solvent removed (Rotovap) to give 8.40 g (89.4%) of the crude product. Distillation at 182° (0.55 mm) gave 7.53 g (76.1%) of the sulfonyl chloride, **7** ($R = C_{10}H_{21}$).

4-*n*-Pentylbenzenethiol, 6 ($R = C_5H_{11}$)

To a stirred mixture of 50 g (0.20 m) of 4-*n*-pentylbenzenesulfonyl chloride in 80 ml concd H_2SO_4 + 500 ml H_2O at <0° was added 72.2 g Zn dust at a rate that this temperature was maintained. Stirring was continued at <0° for 45 min followed by refluxing for 3 hr. The cooled reaction mixture was poured into 600 ml ice cold H_2O and extracted with 2 × 1*l* Et_2O. The combined Et_2O extracts were washed twice with H_2O, filtered (hard paper) to remove some insoluble material, dried, filtered and the solvent removed (Rotovap) to give 33.9 g (92.1%) of a yellow liquid. Distillation at 89–93° (0.6 mm) gave 22.9 g (68.2%) of the thiol **6** ($R = C_5H_{11}$); tlc (CCl_4) showed one spot with $R_f = 0.57$ (sulfonyl chloride $R_f = 0.26$, disulfide $R_f = 0.67$); ir (film) 2570 cm^{-1} (SH, medium) and no SO_2Cl peaks; nmr (CCl_4, Figure 6) 7.06 (split d, 2, $J = 2$ and 8 Hz, ArH *ortho* to SH), 6.88 (split d, 2, $J = 2$ and 8 Hz, ArH *ortho* to alkyl), 3.12 (s, 1, SH), 2.48 (t, 2, $ArCH_2$) and 1.90 – 0.60 (m, 9, C_4H_9); and m/e (rel intensity) 180 (M^+, 31.8%) and 123 ($M—C_4H_9$, 100%).

Anal Calcd. for $C_{11}H_{16}S$: C, 73.27; H, 8.95; S, 17.78. Found: C, 73.27; H, 8.88; S, 17.85.

A sample of the pot residue (1 g) was chromatographed on a column of 50 g of silica gel (Davidson, 60–200 mesh) in CCl_4. Elution with CCl_4 gave 680 mg of material believed to be the disulfide **5** ($R = C_5H_{11}$): nmr ($CDCl_3$) 7.42 (d, 2, $J = 8.5$ Hz, ArH *ortho* to *S*), 7.08 (d, 2, $J = 8.5$ Hz, ArH *ortho* to alkyl), 2.58 (*t*, 2, $ArCH_2$) and 2.0 – 0.70 (m, 9, aliph).

4-*n*-Nonylphenol, 4 ($R = C_9H_{19}$)

A hand stirred by melt of potassium 4-*n*-nonylbenzenesulfonate (20.0 g, 60.0 mmoles) in KOH (39.0 g, 0.69 m) was heated at 320–325° for 10 min in an Armco sheet iron pot. The hot melt was poured cautiously onto ~80 ml cracked ice, the mixture acidified with concd. H_2SO_4 and then extracted with 2 × 80 ml Et_2O. The organic layer was filtered to remove an insoluble tan solid, dried and the solvent removed (Rotovap) to give 8.5 g (62.0%) of the crude phenol. Extraction of a soln of the dried tan solid in 50 ml H_2O with Et_2O gave an additional 400 mg of the phenol (total yield = 65.0%). Distillation at 154–156° (2.4 mm) gave 7.1 g (51.8%) of the phenol, **4** ($R = C_9H_{19}$): mp 43–45° (lit[28] mp 42.5°); tlc ($CHCl_3$) showed one spot with $R_f = 0.20$ (4-ethylphenol, $R_f = 0.15$) and ir ($CHCl_3$) 3350, 3600 (OH) and no

SO_3^- peaks. Nmr ($CDCl_3$) for **7** ($R = C_{10}H_{21}$) δ7.0 (d, 2, J = 7.0 Hz, ArH *ortho* to OH), 6.75 (d, 2, J = 7.0 Hz, ArH *ortho* to alkyl), 5.3–4.3 (s, 1, OH), 2.5 (*t*, 2, J = 4.0 Hz, $ArCH_2$) and 1.82–0.55 (m, 19, C_8H_{17}).

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