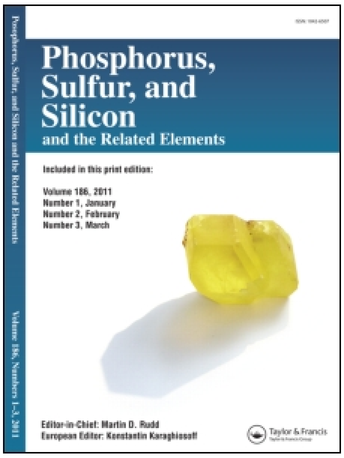

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STUDIES IN THE HETEROCYCLIC COMPOUNDS: I. SOME 2-THIOPHENESULFONYL DERIVATIVES

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STUDIES IN THE HETEROCYCLIC COMPOUNDS: I. SOME 2-THIOPHENESULFONYL DERIVATIVES

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2-Thiophenesulfonyl chloride, prepared by treating thiophene with chlorosulfonic acid, has been condensed with nucleophilic reagents; ammonia, cyclohexylamine, N-methylaniline and sodium azide to afford the sulfonamide, N-cyclohexyl sulfonamide, N,N-methylphenyl sulfonamide and the sulfonyl azide respectively. The sulfonyl azide has been reacted with triphenylphosphine, tri-n-butylphosphine, norbonene and cyclohexene. The ir and nmr spectral characteristics of the products are very briefly discussed.

INTRODUCTION

Sulfonyl compounds are a group of very important organic compounds which exhibit biological as well as pharmacological activities. For example, sulfono hydrazides[1–3] and sulfonamides[4] are known to show fungicidal activities and nematicadal activity has been observed in case of some sulfonyl azides.[5] Also, some heteroaromatic sulfonyl derviatives (including thiophenesulfonyl derivatives) have been shown to have some antifungal and antibacterial activities.[6] From the literature, it appears that the synthesis and reactions of thiophenesulfonyl azide have not been reported. This paper describes the synthesis of thiophenesulfonyl azide and some of its reactions together with a brief description of the ir and nmr spectra of some of the sulfonyl derivatives.

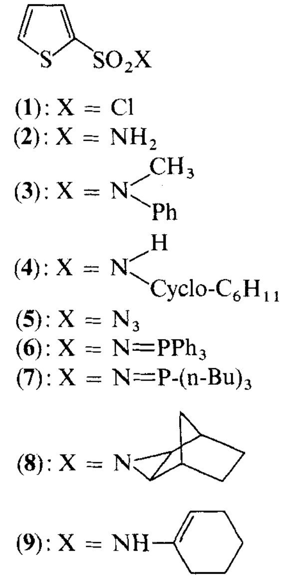

FIGURE 1 Compounds synthesized and studied.

DISCUSSION

Treatment of thiophene with chlorosulfonic acid afforded 2-thiophenesulfonyl chloride (**1**).[7] The sulfonyl chloride was reacted with some nucleophilic reagents: ammonia, N-methylaniline, cyclohexylamine and sodium azide to give the amides (**2**), (**3**), (**4**) and sulfonyl azide (**5**) respectively (Figure 1). The sulfonyl azide also undergoes the following reactions typical of other aromatic sulfonyl azides:[5,8,9] with triphenyl phosphine, it reacted to give the imino-phosphorane (**6**) and also with tri-*n*-butylphosphine to afford a brown oil whose analysis (i.r., nmr and ms) fit the expected imino-phosphorane (**7**). The azide also undergoes the 1,3-dipolar addition reaction[5,8] with norbonene to give the aziridine (**8**). With cyclohexene, the azide gave a product whose elemental analysis, ir, nmr and ms showed it to be thiophene sulfonamide(**2**).

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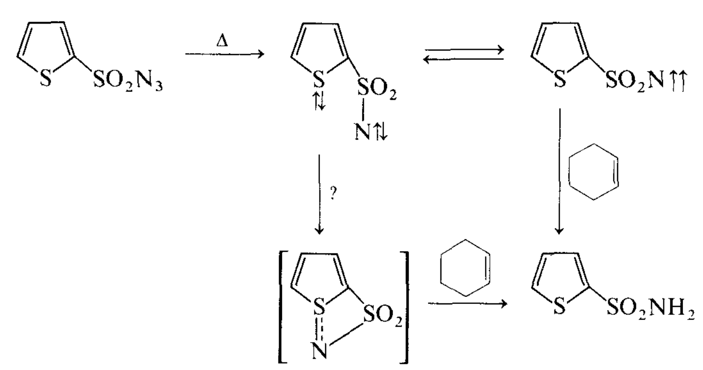

FIGURE 2 Reaction of 2-thiophenesulfonyl Azide with cyclohexene at 140°.

The formation of the sulfonamide (**2**), from the reaction of the sulfonyl azide with cyclohexene could be explained in terms of the intermediate formation of thiophene sulfonyl nitrene,[10] formed by the decomposition of the starting sulfonyl azide followed by a hydrogen abstraction from the cyclohexene (Figure 2).

Hydrogen abstraction has been known to be an important side-reaction-path for sulfonyl nitrenes[11] and for metal-catalyzed thermal decomposition of sulfonyl azides.[12,13] As shown in Figure 2, an interaction between the sulfur atom and the nitrogen nitrene could probably account for the high yield of the sulfonamide.[14] The ir spectra of the various 2-thiophenesulfonyl derivatives showed absorptions in the regions 2105 cm^{-1} and 1520–1510 cm^{-1} due, respectively, to C—H and C—C ring stretching vibrations. Other absorptions in the regions 1400 cm^{-1} and 1213–1220 cm^{-1} are also probably due to the thiophene ring modes.[15a,b,c] The absorptions due to the stretching vibrations of the SO_2, NH_2, —NH and N_3 groups showed in the range that are in accord to literature data and are given in the experimental section.

In the nmr spectra, the thiophene protons of the compounds (**2**), (**4**), (**6**) and (**7**) showed as multiplets centred at δ7.67 and a second multiplet centred around δ7.1 with integral ratio 2:1 whereas in the sulfonyl azide (**5**), the thiophene protons appeared as a doublet centred at δ7.75 and a quartet at δ7.2 with integral ratio 2:1. Other data on nmr are given in the experimental section.

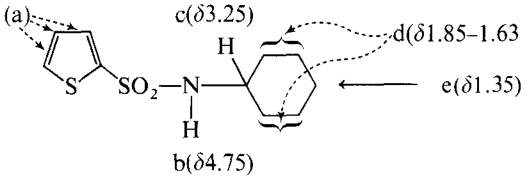

FIGURE 3 Assignments of the protons in the ^1H nmr spectrum of N-cyclohexyl-2-thiophenesulfonamide.

EXPERIMENTAL

Ir spectra were determined in KBr discs or as neat films using a Perkin-Elmer 727B spectrometer. Nmr spectra were measured with a Varian T60 spectrometer in deuterated chloroform or deuterated acetone as appropriate using tetramethylsilane as internal standard. Mass spectra were determined with an AEI MS12 spectrometer at 70eV. Melting points were determined on a Gallenkamp mp apparatus and are uncorrected. Elemental analysis were carried out by Mr. Bob Teed of the Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Canada.

2-Thiophenesulfonyl chloride (**1**). This was prepared according to literature procedure.[16] mp 31–33° (lit[17] 31.5–33°): δ ($CDCl_3$) 7.68–7.88 (2H, m, H_3 and H_5),[18] 6.98–7.25 (1H, m, H_4): m/e 182, 184 (M, 28.0%, 11%), 147 (M-Cl, 96%), 99 (M-Cl-SO, 34%), 57 (M-Cl-SO_2-C_2H_2, 37%), 45 (CSH^+, 43%), and 39 ($C_3H_3^+$, B). ν_{max} 1370. 1165 (SO_2) cm^{-1}.

2-Thiophenesulfonamide (*2*). This was prepared from 1 and excess ammonium hydroxide in ethanol. m.p. 145–147° (lit[17], 147°): δ (CD_3COCD_3) 7.8–7.6 (2H, m, H_5 and H_3), 7.17–7.03 (1H, m, H_4), 6.67 br (2H, SO_2NH_2). The signal at δ 6.67 was removed after D_2O treatment: m/e 163 (M, 48%), 147 (M-NH_2, 55%), 99 (M-NH_2-SO, 43%), 57 (M-SO_2NH_2-C_2H_2, 32%), 45 (CSH^+, 36%) and 39 ($C_3H_3^+$, B). ν_{max} 3320, 3240 (NH_2), 1320, 1155 (SO_2) cm^{-1}.

N,N - Methylphenyl - 2 - thiophenesulfonamide (**3**). 2 - thiophenesulfonyl chloride (1 g) was refluxed with M-methylaniline (2 mol. equivs.) in acetonitrile for 5 hr to give the methylphenylsulfonamide (60%, from petroleum ether 30–60°), mp 105–106°. (Found: C, 52.1; H, 4.7; N, 5.5. $C_{11}H_{11}NO_2S_2$ requires C, 52.2; H, 4.3; N, 5.5%). δ ($CDCl_3$) 7.68–7.0 (8H, m, aromatic protons), 3.18 (3H, s, N-CH_3). m/e 253 (M, 12%), 189 (M-SO_2, 38%), 106 (PhMeN, B), 77 (Ph, 87%) and 39 ($C_3H_3^+$, 65%). ν_{max} 1340, 1155 (SO_2) cm^{-1}.

N - cyclohexyl - 2 - thiophenesulfonamide (**4**). 2-thiophenesulfonyl chloride (2g) was reacted with cyclohexylamine (2mol. equiv.) in acetonitrile 4h to give N-cyclohexylsulfonamide (55%, from petroleum ether) mp 86–88°. (Found: C, 49.1; H, 6.4; N, 5.8. $C_{10}H_{15}NO_2S_2$ requires C, 49.0; H, 6.1; N, 5.7). m/e 245 (M, 20%), 202 (M-43, 59%), 147 (M-NH-C_6H_{11}, 74%), 99 (M-NH-C_6H_{11}-SO, 27%) and 39 ($C_3H_3^+$): ν_{max} 3245 (NH), 1330, 1160 (SO_2) cm^{-1}. In the nmr, in addition to the multiplets in the aromatic region (a), there appeared a doublet, (b), centred at δ 4.75, a poorly resolved multiplet, (c), centred at δ 3.25, a multiplet, (d), lying between δ 1.85 and 1.163 and another multiplet, (e), centred at δ 1.35. The integral ratios a:b:c:(d + e) = 3:1:1:10. The doublet (b) disappeared on shaking with D_2O thus confirming the presence of the -NH group. The various assignments are as shown in Figure 3.

2 - thiophene - sulfonyl azide (**5**). 2 - thiophenesulfonyl chloride (10g) was reacted with sodium azide (7.1g, 2mol. equiv.) in aqueous acetone for 6 hr to give the sulfonyl azide (8.8g, 85%), mp 31–33°. (Found: C, 25.4; H, 1.8; N, 22.3. $C_4H_3N_3O_2S_2$ requires C, 25.4; H, 1.6; N, 22.2). δ ($CDCl_3$) 7.79–7.72 (2H, d, H_3 and H_5), 7.27–7.07 (1H, q, H_4). m/e 189 (M, 11%), 147 (M-N_3, 59%), 99 (M-N_3-SO, 28%), 57 (M-SO_2N_3-C_2H_2, 30%), 45 (CSH^+, 46%) and 39 ($C_3H_3^+$, B). ν_{max} 2140 (N_3), 1375, 1165 (SO_2) cm^{-1}.

Reactions of 2 - thiophenesulfonyl azide (**5**). (i) With triphenylphosphine. 2-thiophenesulfonyl azide (1g) was dissolved in ether (15ml) and added dropwise to triphenylphosphine (1.4g, 1mol. equiv.) in ether (25ml). Some precipitate was formed during the addition. The mixture was refluxed for 5h during which more precipitate was formed. The solution was cooled and the ether decanted. Recrystallization from $CHCl_3$/EtOH, 1:50, gave triphenyl (2-thiophenesulfonylimino) - phosphorane (1.6g, 70%), mp 152–153° (decomp). (Found: C, 62.3; H, 4.6; N, 3.3. $C_{22}H_{18}NO_2PS_2$ requires C, 62.4; H, 4.3; N, 3.3). m/e 423 (M, 12%), 359 (M-SO_2, B), 183 (thiophene-$SO_2NH_2^+$ 46%), 77 (Ph, 57%) and 39 ($C_3H_3^+$, 62%). ν_{max} 1440, 990 (P-Ph), 1340, 1160 (SO_2) cm^{-1}.

ii) With norbornene. The azide (**5**), (1 g), was dissolved in ether (10ml) and added dropwise to norbornene (0.5g); 1mol. equiv.) in ether (6ml) and the mixture refluxed for 24hr. Removal of the ether afforded a solid which recrystallized from EtOH to give the aziridine (**8**), (0.54g; 40%), mp 80–82°. (Found: C, 51.7; H, 5.5; N, 5.5. $C_{11}H_{13}NO_2S_2$ requires C, 51.8; H, 5.1; N, 5.5). ν_{max} 1375, 1155 (SO_2) cm^{-1}. Mass spectrum showed the molecular ion (M^+, 255).

iii) With cyclohexene. 2-thiophenesulfonyl azide (1g) was heated under reflux with cyclohexene (20ml) for 12h at 140°. Removal of the excess cyclohexene gave a solid residue, and recrystallization from aqueous ethanol afforded 2-thiophenesulfonamide (**2**), (0.69g; 80%) mp 142–145° (lit[17] 147°). Its nmr, ir, elemental analysis and mass spectrum are all identical with the product from the reaction of the sulfonyl chloride and ammonium hydroxide. Apparently, no enamine (**9**) was formed as evidenced by the absence of the N-H stretching vibration in its ir spectrum and absence of any SO_2NH proton resonance in its nmr expected in the range for amidic protons δ (9.4–6.0).[9]

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