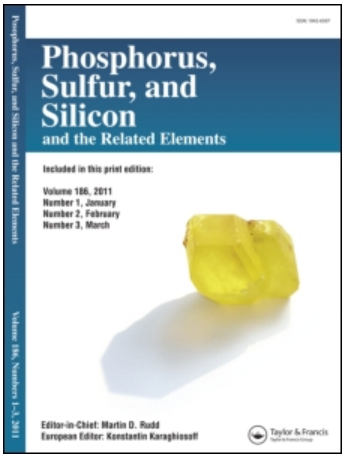

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NEW DECARBOXYLATIVE SULFANYLATION OF SOME PHENYLSULFONYL ARYLACETIC ACIDS

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The reaction of some α-phenylsulfonyl arylacetic acids with NaH in DMSO and dimethyl disulfide leading to α-sulfanylated benzyl phenyl sulfones is discussed.

Keywords: Sulfanylation; decarboxylation; α-sulfonyl α-arylcarboxylic acids; sulfones

INTRODUCTION

The base catalyzed decarboxylation of the α-phenylsulfonyl substituted carboxylic acids in protic medium have been extensively investigated.[1–5] Proofs were provided that the intermediate α-sulfonyl carbanions undergo protonation to give sulfones and that, in the case of the optically active derivatives, the original configuration of the carbon atom is maintained.

The halogenative decarboxylation in aprotic medium in the absence of base was reported by Bordwell[6] for some α-phenylsulfonyl carboxylic acids, which by reaction with halosuccinimides in refluxing CCl_4, afforded the corresponding α-halo sulfones. Our recent studies[7,8] of the reactions of α-phenylsulfonyl α-alkylsubstituted carboxylic acids with sulfanylating agents in aprotic medium showed that the decarboxylation takes place only in the sulfanylated product during the work-up and therefore in protic medium.

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This communication presents the results of decarboxylative sulfanylation of some α-phenylsulfonyl arylacetic acids in the aprotic medium.

RESULTS AND DISCUSSION

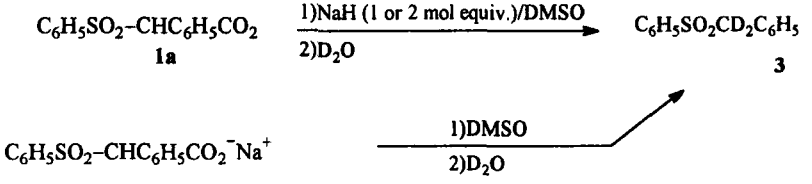
Three α-phenylsulfonyl substituted carboxylic acids: phenylacetic **1a**, 4-methoxyphenylacetic **1b** and α-phenylpropionic **1c** were submitted to reaction with NaH/DMSO, followed by addition of dimethyl disulfide, at r.t. (Table I). While the acids **1a, b** afforded the corresponding sulfanylated sulfones (**2a, b**), the acid **1c** yielded the unsulfanylated sulfone **2c**.

TABLE I Sulfanylation of some α-phenylsulfonyl α-aryl carboxylic acids*

	$C_6H_5SO_2$-CRR'CO_2H		$C_6H_5SO_2$-CRR'SMe
	1		*2*
	R	*R'*	*% Yields (isolated)*
a	H	C_6H_5	70[12]
b	H	p-MeOC_6H_4	55[12]
c	Me	C_6H_5	70**[13]

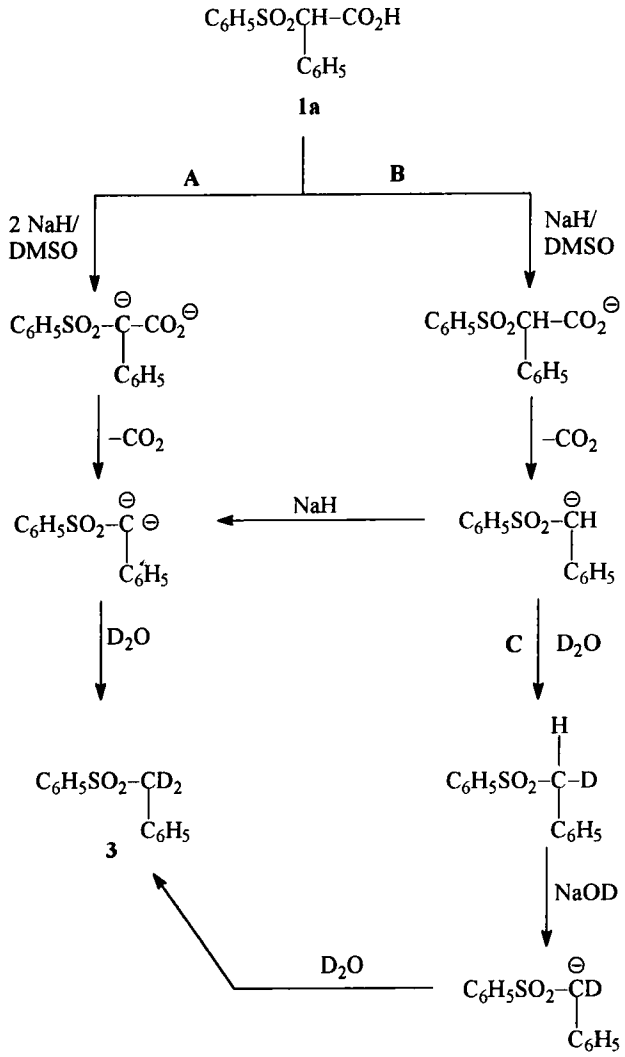
*NaH (1 or 2 equiv.)/DMSO/MeSSMe, r.t.;
**$C_6H_5SO_2$CRR'H.

In order to obtain an insight into the sequence of steps for these sulfanylative decarboxylations, some deuteriation experiments were performed. It was verified that when the α-phenylsulfonyl phenylacetic acid **1a** in DMSO was treated with 2 mol equiv. of NaH, followed by addition of D_2O, the corresponding dideuterio sulfone **3** was obtained. However, surprisely, the same result was obtained when either 1 mol equiv. of NaH was employed or when D_2O was added to the solution of the sodium salt of the same acid in DMSO (Scheme 1).



SCHEME 1

Two alternative mechanisms **A** or **B** can be advanced to account for the reaction of the acid **1a** with 2 mol equiv. of NaH, leading in both cases to the formation of the dideuterio sulfone **3** via the gem dianion. A third pathway **C** may be proposed to explain the formation of the same product **3** when 1 mol equiv. of NaH was used (Scheme 2).



SCHEME 2

The formation of the dideuterated sulfone **3**, followed by ^{1}HNMR, when the sodium carboxylate was dissolved in DMSO and treated with D_2O, is a strong indication that in the case of 2 equiv. of NaH, mechanism **B** is operating.

It seems reasonable to suggest that in the course of the process of sulfanylation, the decarboxylation occurs at the initial stage to give, in the case of 1 equiv. of NaH, the α-sulfonyl carbanion which then undergoes sulfanylation. It should be mentioned that the formation of the sulfanylated anion, in the case of 2 equiv. of NaH, does not lead to the disulfanylated product, even when an excess of sulfanylating agent is employed, most probably due to steric reasons (Scheme 3). Similar explanation can be given for the lack of reactivity of the α-phenylpropionic acid **1c**, which did not undergo sulfanylation but only decarboxylation (Table I). It is noteworthy that the phenyl α-methyl benzyl sulfone **2c** also remained unchanged when treated with NaH/DMSO and dimethyl desulfide.

In summary, the first case of reaction of α-phenylsulfonyl carbanions, generated by decarboxylation of the corresponding carboxylic acids, with the sulfur electrophile, is described.

EXPERIMENTAL

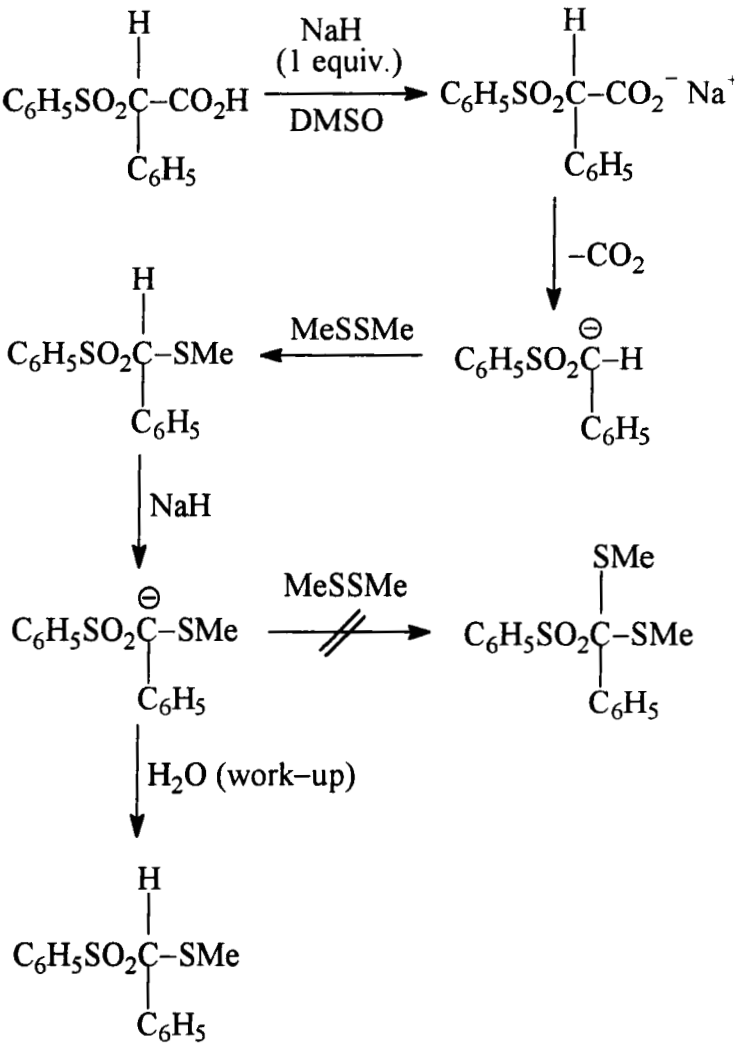
^{1}HNMR spectra were recorded on a Bruker AC-200 spectrometer, using tetramethylsilane as internal standard. Elemental analyses were performed using a Perkin Elmer 2400 CHN elemental analyser. All melting points are uncorrected and were determined using an Electrothermal IA 9100 instrument.

α-Benzenesulfonyl-phenylacetic acid (1a)

Was prepared according to literature procedure,[9] by metalation of phenyl benzylsulfone with n-butyllithium, followed by carbonation and hydrolysis.

α-Benzenesulfonyl-α-phenylpropionic acid (1c)

Was prepared by methylation of the corresponding ester and subsequent hydrolysis as follows:



SCHEME 3

To a magnetically stirred suspension of sodium hydride (95%; 0.87 g; 34 mmol) in dry DMSO (5 mL), was added, under nitrogen and via syringe, a solution of ethyl α-benzenesulfonyl-phenylacetate[10] (7.0 g, 23 mmol) in dry DMSO (12 mL). After cessation of gas evolution, a solu-

tion of methyl iodide (9.8 mL, 69 mmol) in dry DMSO (5 mL) was slowly added via seringe. After stirring 4 h at r.t., the reaction mixture was poured into saturated aqueous ammonium chloride (100 mL) and extracted with dichloromethane (4 × 30 mL). The combined organic extract was washed with aqueous sodium thiosulfate (2 × 20 mL), water (2 × 30 mL), dried over $MgSO_4$, and concentrated under vacuum. The resulting crude yellow oil (6.9 g, 94% yield) required no further purification. Anal. calcd. for $C_{17}H_{18}SO_4$: C 64.13, H 5.70. Found: C 64.28, H 5.55. ^{1}H NMR ($CDCl_3$, δ) 1.26 (t, 3H), 2.11 (s, 3H), 4.24 (dq, 2H), 7.21–7.48 (m, 10H). A mixture of the crude ester (3.2 g, 10 mmol) and potassium hydroxide (1.2 g, 21 mmol), dissolved in 20 mL of 95% ethanol, was magnetically stirred for 3h at 40°C. The solvent was removed under vacuum and the residue was treated with ice water and HCl (15%) until pH = 2. After extraction with dichloromethane, drying ($MgSO_4$) and concentration, the resulting white solid was washed with cold diethyl ether, affording 1.4 g (48%) yield of pure solid acid (m.p. 115.0–116.4°C decomp.). Anal. calcd. for $C_{14}H_{14}SO_4$: C 62.05, H 4.86. Found: C 61.97, H 5.02. ^{1}H NMR (DMSO-d_6, δ) 2.27 (s, 3H), 7.29–7.72 (m, 10H) 8.13 (s, 1H).

α-Benzenesulfonyl-(p-methoxyphenyl)acetic acid (1b)

Was prepared by hydrolysis of the corresponding ester, as follows:

A solution of ethyl α-bromo-(p-methoxyphenyl)acetate[11] (10.0 g, 36.6 mmol) and sodium benzenesulfinate (6.0 g, 37 mmol) in ethanol (95%, 100 mL) was stirred under reflux for 12 h. After standing overnight, the excess of ethanol was distilled off. The residue was poured into water. The oily layer was dissolved in dichloromethane and the aqueous solution was extracted with the same solvent. The combined organic extract was washed with water and dried over $MgSO_4$. After removal of solvent the resulting orange solid was crystallised from ethanol/water, yielding 7.5 g (61% yield) of a white solid (m.p. 80.2–81.2°C) identified as ethyl α-benzenesulfonyl-(p-methoxyphenyl)acetate. Anal. calcd. for $C_{17}H_{18}SO_5$: C 61.06, H 5.43. Found C 60.88, H 5.48. ^{1}H NMR ($CDCl_3$, δ) 1,22 (t, 3H), 3.80 (s, 3H), 4.16–4.26 (m, 2H), 5.05 (s, 1H) and 6.79–7.65 (m, 9H). A mixture of pure ester (3.0 g, 9.0 mmol) and potassium hydroxide (1.1 g, 19 mmol), dissolved in 20 mL of 95% ethanol, was magnetically stirred for 12 h, at r.t. The solvent was removed under vacuum and the residue was treated with ice water and HCl (15%) until pH = 2. After extraction

with dichloromethane, drying ($MgSO_4$) and concentration, the resulting white solid was crystallised from chloroform/hexane, yielding 1.7 g (62% yield) of a white solid (m.p. 159.3–160.7°C) identified as **1b**. Anal. calcd. for $C_{14}H_{14}SO_5$: C 58.81, H 4.60. Found: C 58.34, H 4.55. ^1H NMR (acetone d-6, δ) 3.79 (s, 3H), 5.10 (s, 1H), 6.75 (d, 2H), 7.31 (d, 2H) and 7.44–7.69 (m, 5H).

Sulfanylation of α-benzenesulfonyl α-aryl carboxylic acids

Typical procedure: To a magnetically stirred suspension of sodium hydride (95%, 0.10 g, 3.9 mmol) in dry DMSO (4 mL), under nitrogen, was added, via syringe, a solution of α-benzenesulfonyl-phenylacetic acid **1a** (1.00 g, 3.62 mmol) in 5 mL of dry DMSO. After cessation of gas evolution, a solution of dimethyl disulfide (0.52 g, 4.34 mmol) in dry DMSO (2 mL) was added slowly via syringe. After stirring for 1 h the mixture was poured into water (150 mL) and acidified to pH = 2 with aqueous HCl (15%). The suspended orange solid was filtered and crystallised from carbon tetrachloride/hexane, yielding 0.70 g (70% yield) of α-methylsulfanylbenzyl phenylsulfone **2a**.[12]

Acknowledgements

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