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Lithio Styryl Sulfone as an Acyl Anion Synthon

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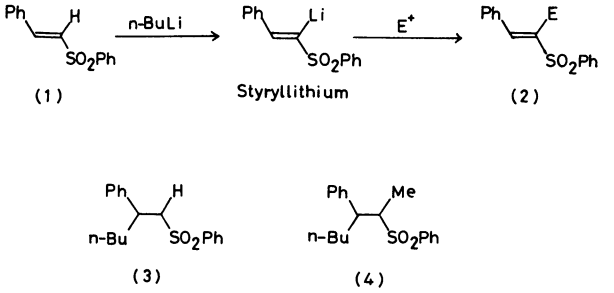
Synopsis. Lithio styryl sulfone, which was shown to be an acyl anion synthon, reacted with various electrophiles; the products were rearranged by treatments with *m*-chloroperbenzoic acid to give acyl benzyl sulfones in good yields.

Recents reports concerning reactions of vinyl anions (especially α-vinyl anions activated with such heteroatoms as oxygen,[1] sulfur,[2] nitrogen,[3] silicon,[4] halogen,[5] or selenium[6]) showed that these anions serve as useful synthons for organic syntheses.

Here, we wish to report on a method for the formation and the reaction of lithio styryl sulfone and alkylated products (after epoxidation with *m*-chloroperbenzoic acid (*m*-CPBA)) rearranged to acyl benzyl sulfones in good yields.



Scheme 1.

(*E*)-Phenyl styryl sulfone (**1**) was lithiated at the β-styryl position regioselectively with butyllithium in tetrahydrofuran (THF) at −78 °C under nitrogen. Styryllithium is stable below −50 °C for several hours, but above −15 °C it gradually decomposes. Styryllithium reacted smoothly with methyl iodide between −78 and −50 °C to give (*E*)-1-phenyl-2-phenylsulfonyl-1-propene (**2a**), mp 91—92 °C (lit,[7] mp 90—93.5 °C) in 92% yield. The reaction was highly regioselective and only the β-methylated product **2a** was obtained. Although this styryl sulfone system has the property that it tends to serve as a Michael acceptor for bases[8] and organometallics,[9] none of **3** or **4** could be detected in a reaction of styryllithium with methyl iodide.[2b]

Styryllithium was allowed to react with various electrophiles to give the corresponding products in good yields (Table 1).

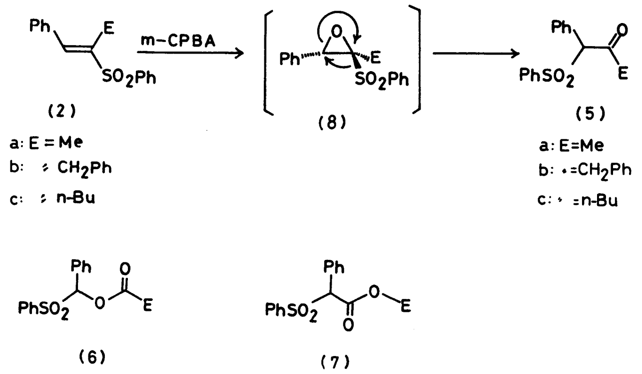
Alkylated styryl sulfone (**2a**) was treated with 3 equivalents of *m*-CPBA in refluxing carbon tetrachloride for 48 h to give 1-phenyl-1-phenylsulfonyl-2-propanone (**5a**), mp 120—122 °C (lit,[10] mp 122—123 °C) in 82% yield. In this reaction none of the Baeyer–Villiger oxidation product (**6** or **7**) was detected.

In the mechanism for the formation of **5a** from **2a**, it is considered that upon a treatment of **2a** with *m*-CPBA, epoxy sulfone (**8**) is initially formed as an unstable intermediate and then rearranged to an acyl compound **5a**, as illustrated in Scheme 2.[11,12]

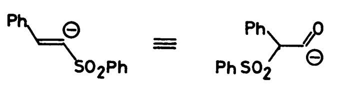
Table 1. The reaction of Styryllithium with Various Electrophiles

Entry	Electrophile	Yield/%
a	MeI	92
b	$PhCH_2Br$	90[a]
c	*n*-BuI	88[a]
d	PhCOCl	89[a]
e	$(n\text{-Bu})_3SnCl$	85[b]

a) Same reaction condition as general procedure A. b) In addition to the reaction condition of general procedure A, 10 mmol of tetramethylethylenediamine (TMEDA) was used as a stabilizer of styryllithium.



Scheme 2.



Scheme 3.

Styryl sulfones **2b** and **2c** were also allowed to become oxidatively rearranged to the corresponding products: **5b** (75%) and **5c** (72%).

By combining this regioselective alkylation and oxidative rearrangement, it is obvious that lithio phenyl styryl sulfone is a masked acyl anion synthon (Scheme 3). Furthermore, the sulfonyl group can be easily removed from the sulfone (**5**) to obtain an olefin; it can also be reductively removed to form a saturated acyl compound, indicating that this method is useful in organic syntheses.

Experimental

(*E*)-Phenyl Styryl Sulfone (1): Compound 1 was synthesized from methyl phenyl sulfone with benzaldehyde in the presence of a base and a phase-transfer catalyst.[13]

Formation and Reaction of Lithio Styryl Sulfone: General Procedure A: To a stirred solution of 1 (2.44 g, 10 mmol) in 60 ml of dry THF, 6.3 ml (10 mmol) of *n*-BuLi (1.6 mol solution in hexane) was added dropwise within 5 min at −78 °C under a nitrogen atmosphere. After 30 min styryllithium was formed as a red solution.

To this red solution 1.42 g (10 mmol) of methyl iodide in dry THF (5 ml) was added dropwise, continuously stirred at −78—−50 °C for 1 h and then warmed to room temperature within 30 min. The reaction mixture was quenched with water and neutralized with diluted hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated. The crude product was purified by silica-gel column chromatography with benzene to give a crystalline product **2a** (2.37 g, 92%), mp 91—92 °C (lit,[7] mp 90—93.5 °C). ^{1}H NMR (CCl_4) δ=2.04 (d, 3H), 7.30 (s, 5H), 7.50 (m, 3H), 7.8—8.0 (m, 3H). MS *m/z* 258 (M^+).

Test of the Stability of Styryllithium: The lithio compound was formed by the general procedure A; then, the solution was warmed to −15 °C in an ice-salt bath. After 15 min stirring at −15 °C an equimolar amount of methyl iodide was added dropwise and the reaction mixture was treated by general procedure A. Only 24% of **2a** was detected.

Compound **2b—e** was synthesized by general procedure A.

2b: Mp 143.5—145.5 °C (from EtOH). ^{1}H NMR ($CDCl_3$) δ=4.05 (s, 2H), 7.06 (s, 5H), 7.38 (m, 8H), 7.74 (m, 2H), 8.13 (s, 1H). Found: C; 75.43, H; 5.46% Calcd for $C_{21}H_{18}O_2S$; C; 75.42, H; 5.42%.

2c: Oil ^{1}H NMR (CCl_4) δ=0.68—1.60 (m, 7H), 2.32 (m, 2H), 6.90—7.90 (m, 11H).

2d: Mp 136—137 °C (from EtOH) (Lit,[14] mp 137—138 °C). IR (neat) 1670 (C=O), 1310 and 1150 cm^{-1} (SO_2).

2e: Oil NMR (CCl_4) 0.62—1.60 (m, 27H), 7.28 (s, 5H), 7.51 (m, 3H), 7.85 (m, 2H), 7.83 (s, 1H).

1-Phenyl-1-phenylsulfonyl-2-propanone (5a): General Procedure B: The mixture of **2a** (318 mg, 1.16 mmol) and *m*-CPBA (600 mg, 3.48 mmol) in CCl_4 (10 ml) was refluxed for 48 h under nitrogen. The reaction mixture was then washed with a diluted sodium hydrogencarbonate solution three times and with a diluted sodium hydrogensulfite solution. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was worked up as usual and the obtained residue was purified by silica gel column chromatography with benzene-ethyl acetate (19 : 1) to give crystalline product **5a** in 82% (260 mg) yield. Mp 120—122 °C (lit,[10] mp 122—123 °C). ^{1}H NMR ($CDCl_3$) δ=2.30 (s, 3H), 5.29 (s, 1H), 7.19 (s, 5H), 7.3—7.7 (m, 5H). IR ($CHCl_3$) 1730 (C=O), 1310 and 1150 cm^{-1} (SO_2). MS *m/z* 274 (M^+, 25), 232 (M^+−CH_2CO, 100).

According to general procedure B, compound **5b** and **5c** were synthesized.

5b: Mp 145—145.5 °C (from benzene). ^{1}H NMR ($CDCl_3$) δ=4.00 (s, 1H), 7.00 (s, 5H), 7.1—7.5 (m, 8H), 7.70 (m, 2H), 8.10 (s, 1H). MS *m/z* 192 (M−$PhSO_3H$, 100), 91 ($PhCH_2^+$, 72). Found: C; 71.86, H; 5.15%. Calcd for $C_{21}H_{18}O_3S$: C; 71.98, H; 5.18%.

5c: Oil ^{1}H NMR ($CDCl_3$) δ=0.85 (m, 3H), 1.00—1.60 (m, 4H), 2.65 (t, 2H), 5.24 (s, 1H), 7.3—8.2 (M, 10H). IR ($CHCl_3$) 1730 cm^{-1} (C=O)

Oxidation of 2d: Compound (**2d**) (500 mg, 1.44 mmol) and *m*-CPBA (496 mg, 2.88 mmol) in 15 ml of CCl_4 were refluxed for 24 h. The reaction mixture was then treated as general procedure B. Benzoic acid (81 mg), mp 120—122 °C (lit,[15] mp 122.4 °C) was obtained and the starting material **2d** (308 mg, 62%) was recovered. Both compounds could be identified by their NMR spectra, compared with those of known samples.

Oxidation of 2e: Compound **2e** (250 mg, 0.47 mmol) and *m*-CPBA (162 mg, 0.94 mmol) in 7 ml of CCl_4 were refluxed for 24 h. The reaction mixture was treated by general procedure B. Phenyl styryl sulfone (**1**) (61 mg, 53%) and an unknown product (92 mg) (NMR spectrum of this product in CCl_4 showed at 0.7—1.8 ppm.) were obtained. In this reaction the starting material (**2e**) was not recovered.

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