A New Synthesis of Alkynyl Sulfones and Single Crystal X-ray Structure of *p*-(Tolylsulfonyl)ethyne

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Received May 14, 1993•

The reaction of mono- or bis(alkynyliodonium) triflate salts with sodium *p*-toluenesulfinate under mild conditions affords alkynyl sulfones in 60–95% yields.

Acetylenic sulfones are used extensively in organic synthesis as activated acetylene equivalents.[1] Typical applications include cycloadditions,[2,3] addition reactions with amines,[4] cuprates,[5] metals,[6] or alkoxides,[7] and substitution reactions with Grignard[8] or organolithium reagents.[8b,9] The products of the cyclization and addition reactions generally possess the vinyl sulfone moiety, which can be easily removed[10,11] or exploited for further synthetic elaboration.[10] Despite their widespread application, few general procedures for the preparation of acetylenic sulfones have been reported. Existing methods of preparation, namely elimination[12] or oxidation[13] procedures, exhibit limited generality and restrict the range of functional groups that can tolerate the reaction conditions. Although the structure and chemistry of sulfones in general have been extensively examined,[14] a literature survey indicated that surprisingly few acetylenic sulfones have been fully characterized. In addition, to our knowledge no X-ray data for acetylenic sulfones are currently available. We now wish to report a new, general, and efficient procedure for the formation of β-alkyl, β-aryl, and β-functionalized acetylenic sulfones in the absence of base or oxidizing agents via the reaction of alkynyliodonium triflates[15–18] with $NaSO_2Ar$ (Ar = *p*-$CH_3C_6H_4$). Furthermore, the characterization of the parent acetylenic sulfone, $HC{\equiv}CSO_2Ar$, by X-ray crystallography is detailed.

Results and Discussion

Our initial attempts toward the formation of acetylenic sulfones from the corresponding alkynyliodonium triflate salts were conducted via aqueous anion exchange. Under these conditions, alkynyl(phenyl)iodonium triflates **1** (Scheme I) are known to undergo rapid exchange between the nucleophile and triflate anion.[19] Subsequent rearrangement of the intermediate ylide **2** with reductive elimination of PhI yields the desired acetylenic sulfones **3** and **5**. The alkynyliodonium salt was shaken in a separatory funnel at 0 °C for approximately 3 min and, following workup, alkynyl sulfones **3a–g** and **5** were obtained in yields of 30–88% (Table I, method A). Attempts to optimize product yields via variation of solvent and reaction conditions revealed that reaction of the alkynyliodonium triflates with anhydrous $NaSO_2Ar$ in CH_2Cl_2 resulted in increased or comparable yields of **3a–h** (Table I, method B). The sole exception to this trend was in the formation of the disulfone **5**, where anhydrous conditions resulted in a decreased yield. Isolation of the resulting sulfones was accomplished via crystallization of **3a–d** and **5** from the reaction mixture following workup or by chromatography for **3e–h**. Assigned structures were completely consistent with ^1H NMR, ^{13}C NMR, EA or HRMS, and published data.

To investigate the structural characteristics of this class of compounds, analysis of the parent alkynyl sulfone, $HC{\equiv}CSO_2Ar$, was conducted via X-ray crystallography.[20a]

• Abstract published in *Advance ACS Abstracts*, August 15, 1993.

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Scheme I

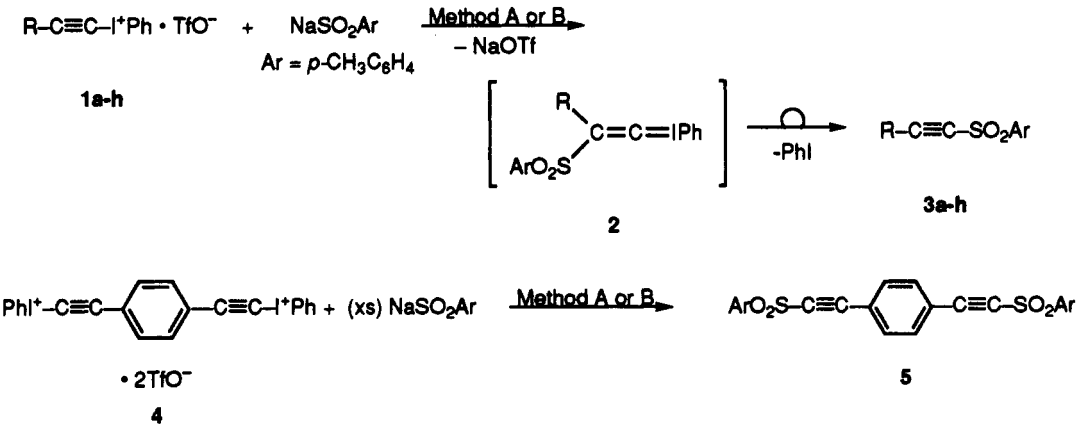

Table I. Alkynyl Sulfones from Alkynyliodonium Triflates

compd	R	% yield method A[a]	% yield method B[b]
3a	H	46	87
3b	CH_3	71	87
3c	*t*-Bu	89	95
3d	Ph	42	78
3e	$(i\text{-Pr})_3Si$	80	79
3f	$ClCH_2$	43	86
3g	$BrCH_2$	31	60
3h	$(CH_3)(Ph)(HO)C$	*c*	81
5	*p*-C_6H_4	88	~15

[a] Reaction carried out in 1:1 CH_2Cl_2/H_2O at 0 °C. [b] Reaction carried out in dry CH_2Cl_2 with anhydrous NaTs at 25 °C. [c] Due to the limited stability of **3h**, only method B was attempted.

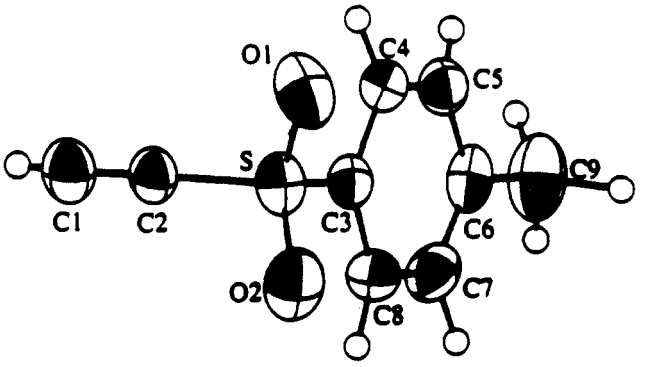

Figure 1. ORTEP of 1-(*p*-tolylsulfonyl)ethyne (**3a**).

The ORTEP structure for **3a** and a summary of key bond lengths and angles are shown in Figures 1 and 2, respectively. As expected, the acetylenic bond is slightly shortened to 1.139 Å and the C≡C–S bond is essentially linear with an angle of 179.3°. The C–S bond length of 1.711 Å, S–Ar bond length of 1.757 Å, C–S–Ar angle of 103.6°, and O=S=O angle of 119.7° are all comparable to other unsaturated sulfones. A direct comparison of **3a** to the crystallographic data of *trans*-1-(*p*-tolylsulfonyl)-propene[20b] reveals little difference in the major bond angles and lengths (Figure 2). The vinyl sulfone C–S bond length of 1.748 Å, S–Ar bond length of 1.766 Å, C–S–Ar angle of 105.3°, and O=S=O angle of 118.8° are essentially identical to those of **3a**.

(20) (a) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (b) Klazinga, A. H.; Vos, A. *Rec. Trav. Chim. Pays-Bas* **1973**, *92*, 360.

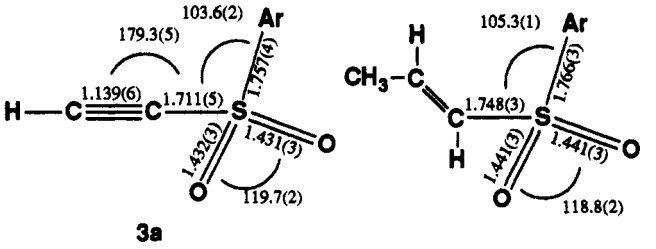

Figure 2. Comparison of key bond angles (deg) and lengths (Å) of **3a** and 1-(*p*-tolylsulfonyl)propene.

In conclusion, we have demonstrated the facile, high-yield formation of alkynyl sulfones via the reaction of alkynyl(phenyl)iodonium triflates with $NaSO_2Ar$. The absence of base and oxidizing agents from the reaction medium permits the incorporation of not only alkyl and aryl substituents, but also halogen and alcohol functionalities. The ready availability and stability of alkynyliodonium salts coupled with the mild reaction conditions make this procedure a valuable alternative to current syntheses of alkynyl sulfones.

Experimental Section

Materials. All commercial reagents were ACS reagent grade and were used without further purification. All solvents were distilled from CaH_2. $PhI^+CN\text{-}OTf$[21] and alkynyl (phenyl)-iodonium triflates **1a–e**,[16] **1f–g**,[17] and **4**[18] were prepared by known methods. Sodium *p*-toluenesulfinate was purchased from Lancaster as the hydrated salt and dried by heating in vacuo at 200 °C for 24 h. The reaction flasks were flame-dried and flushed with N_2 prior to use.

3-Methyl-3-phenyl-1-[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]propyn-3-ol (1h). A solution of 3-methyl-3-phenyl-1-(tributylstannyl)-propyn-3-ol (0.44 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of $PhI^+CN\text{-}OTf$ (0.38 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at −42 °C under N_2 and maintained at this temperature for 45 min. Ether (10 mL) and hexanes (50 mL) were added to the solution, which precipitated a pale yellow oil. The solvents were decanted and the oil was subsequently washed with ether (3 × 30 mL) at 25 °C to give 0.40 g (80%) of **1h** as a pale yellow oil which was stable for several days under refrigeration, but decomposed in 2–3 h at 25 °C neat or in solution: IR (neat) 3414 (OH), 2178 (C≡C), 1280, 1167, 1026 cm^{-1}; ^1H NMR (CD_3CN) δ 8.16 (d, *J* = 7.9 Hz, 2H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.29 (m, 3H), 4.64 (s, 1H, OH), 1.70 (s, 3H); ^{13}C NMR (CD_3CN) δ 144.9, 135.9, 134.1, 133.5, 129.4, 129.0, 125.7, 117.6 (all Ph), 121.6 (q, *J* = 320 Hz, CF_3SO_3), 112.5 (C≡CI), 71.3 (COH), 32.9 (CH_3), 28.3 (C≡*C*I).

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General Procedure for the Synthesis of 1-(*p*-Tolylsulfonyl)alkynes. Method A: A solution of the appropriate alkynyliodonium triflate salt **1a–g** or **5** (0.36–1.32 mmol) in CH_2Cl_2 (35 mL) was shaken with an aqueous solution of sodium *p*-toluenesulfinate (3 equiv in 35 mL of H_2O) at 0 °C for approximately 3 min. The layers were separated and the aqueous phase was extracted once with CH_2Cl_2 (25 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered, and the volume was reduced in vacuo. Addition of hexanes resulted in crystallization of sulfones **3a–d**. Purification of sulfones **3e–g** was achieved via radial chromatography (2 mm, silica 200–400 mesh; CH_2Cl_2/hexanes, 1:1). Bis-sulfone **5** was recrystallized from CH_3CN by the addition of ether and hexanes.

Method B: Anhydrous sodium *p*-toluenesulfinate (1.1 equiv) was added to a stirred solution of the appropriate alkynyliodonium triflate salt **3a–h** or **5** (0.36–6.61 mmol) in CH_2Cl_2 (15–50 mL) at 25 °C and allowed to react until the acetylenic absorption of the iodonium salt was no longer observed (0.25–0.5 h) in the IR spectrum. The reaction mixture was passed through a plug of silica gel (200–400 mesh, 3 g) and concentrated. Purification of sulfones **3a–g** was achieved as in method A and via radial chromatography for **3h** (2 mm, silica 200–400 mesh; Et_2O/hexanes, 1:3).

1-(*p*-Tolylsulfonyl)ethyne (3a). Method A: Reaction of **1a** (0.50 g, 1.32 mmol) with aqueous NaTs (0.71 g, 4.00 mmol, 35 mL) at 0 °C gave 0.11 g (46%) of **3a** as a white solid: mp 73–75 °C, lit.[22] 74–75 °C. **Method B:** Reaction of **1a** (2.50 g, 6.61 mmol) with anhydrous NaTs (1.18 g, 6.65 mmol) gave 1.04 g (87%) of **2a** as a white solid, mp 73–74 °C.

1-(*p*-Tolylsulfonyl)-1-propyne (3b). Method A: Reaction of **1b** (0.50 g, 1.28 mmol) with aqueous NaTs (0.68 g, 3.8 mmol, 35 mL) at 0 °C gave 0.18 g (71%) of **3b** as a white solid: mp 96–98 °C, lit.[23] 98–99 °C. **Method B:** Reaction of **1b** (0.19 g, 0.50 mmol) with anhydrous NaTs (0.10 g, 0.60 mmol) gave 84 mg (87%) of **3a** as a white solid, mp 96–97 °C.

3,3-Dimethyl-1-(*p*-tolylsulfonyl)-1-butyne (3c). Method A: Reaction of **1c** (0.50 g, 1.15 mmol) with aqueous NaTs (0.62 g, 3.5 mmol, 35 mL) at 0 °C gave 0.24 g (89%) of **3c** as a white solid: mp 99–101 °C, lit.[24] 99.5–100.5 °C. **Method B:** Reaction of **1c** (0.22 g, 0.50 mmol) with anhydrous NaTs (0.11 g, 0.60 mmol) gave 0.112 g (95%) of **3c** as a white solid, mp 99–100 °C.

2-Phenyl-1-(*p*-tolylsulfonyl)ethyne (3d). Method A: Reaction of **1d** (0.50 g, 1.10 mmol) with aqueous NaTs (0.59 g, 3.30 mmol, 35 mL) at 0 °C gave 0.12 g (42%) of **3d** as a pale yellow solid, mp 80–81 °C, lit.[25] 80–81 °C. **Method B:** Reaction of **1d** (0.30 g, 0.66 mmol) with anhydrous NaTs (0.14 g, 0.78 mmol) gave 0.131 g (78%) of **3d** as a pale yellow solid, mp 81 °C.

1-(*p*-Tolylsulfonyl)-2-(triisopropylsilyl)ethyne (3e). Method A: Reaction of **1e** (0.30 g, 0.56 mmol, 35 mL) with aqueous NaTs (0.60 g, 3.40 mmol, 35 mL) at 0 °C gave 0.15 g (80%) of **3e** as an oily solid. **Method B:** Reaction of **1e** (0.27 g, 0.50 mmol) with anhydrous NaTs (0.11 g, 0.60 mmol) gave 0.132 g (79%) of **3e** as an oily solid: IR (thin film) 2122, 1338, 1162 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H), 1.05 (sept, J = 5.3 Hz, 3H), 1.01 (d, J = 5.2 Hz, 18H); ^{13}C NMR ($CDCl_3$) δ 145.1, 139.1, 129.8, 127.2 (all Ph), 100.8, 100.0, 21.7 ($ArCH_3$), 18.3 (CH), 10.9 (CH_3); EI HRMS m/z 336.1581 M^+, calcd for $C_{18}H_{28}SiSO_2$ 336.1579.

3-Chloro-1-(*p*-tolylsulfonyl)-1-propyne (3f). Method A: Reaction of **1f** (0.32 g, 0.75 mmol, 35 mL) with aqueous NaTs (0.40 g, 2.25 mmol, 35 mL) at 0 °C gave 73 mg (43%) of **3f** as a white solid, mp 63–64 °C. **Method B:** Reaction of **1f** (0.32 g, 0.75 mmol) with anhydrous NaTs (0.15 g, 0.83 mmol) gave 0.15 g (86%) of **3f** as a white solid, mp 63–64 °C; IR (CCl_4) 3068, 2213 (C≡C), 1339, 1166 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 4.17 (s, 2H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.9, 137.8, 130.0, 127.6 (all Ph), 87.6 (*C*≡CS), 82.3 (C≡*C*S), 28.3 (CH_2), 21.8 (CH_3); EI HRMS m/z 228.0010 M^+, calcd for $C_{10}H_9SClO_2$ 228.0012. Anal. Calcd for $C_{10}H_9SClO_2$: C, 52.52; H, 3.97; S, 14.02. Found: C, 52.58; H, 4.00; S, 13.95.

3-Bromo-1-(*p*-tolylsulfonyl)-1-propyne (3g). Method A: Reaction of **1g** (0.35 g, 0.75 mmol, 35 mL) with aqueous NaTs (0.15 g, 0.83 mmol, 35 mL) at 0 °C gave 63 mg (31%) of **3g** as a white solid, mp 64–65 °C. **Method B:** Reaction of **1g** (0.35 g, 0.75 mmol) with anhydrous NaTs (0.15 g, 0.83 mmol) gave 0.123 g (60%) of **3g** as a white solid, mp 64–65 °C; IR (CCl_4) 3067, 2208 (C≡C), 1327, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.91 (s, 2H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.8, 137.8, 130.0, 127.5 (all Ph), 88.2 (*C*≡CS), 82.1 (C≡*C*S), 21.8 (CH_3), 10.7 (CH_2); EI HRMS m/z 271.9497 M^+, calcd for $C_{10}H_9SBrO_2$ 271.9507. Anal. Calcd for $C_{10}H_9SBrO_2$: C, 43.97; H, 3.32; S, 11.74. Found: C, 44.09; H, 3.34; S, 11.66.

3-Methyl-3-phenyl-1-(*p*-tolylsulfonyl)propyn-3-ol (3h). Method B: Reaction of **1h** (0.35 g, 0.70 mmol) with anhydrous NaTs (0.15 g, 0.84 mmol) gave 0.17 g (81%) of **3h** as a homogeneous clear oil: IR (thin film) 3413 (OH), 3063, 2197 (C≡C), 1340, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 2H), 7.40 (m, 2H), 7.31 (m, 5H), 3.15 (s, 1H, OH), 2.43 (s, 3H, $ArCH_3$), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.6, 142.6, 138.1, 129.9, 128.5, 128.3, 127.3, 124.5 (all Ph), 96.4 (C≡CS), 81.3 (C≡*C*S), 69.9 (*C*OH), 32.0 (CH_3), 21.7 ($ArCH_3$); CI HRMS m/z 301.0879 $(M + 1)^+$, calcd for $C_{17}H_{17}SO_3$ 301.0898.

1,4-Bis[(*p*-tolylsulfonyl)ethynyl]benzene (5). Method A: Reaction of **4** (0.30 g, 0.36 mmol) with aqueous NaTs (0.40 g, 2.16 mmol, 35 mL) at 0 °C gave 0.138 g (88%) of **5** as a pale yellow solid, mp 198–199 °C dec. **Method B:** Reaction of **4** (0.30 g, 0.36 mmol) with anhydrous NaTs (0.072 g, 0.40 mmol), gave ~15% (by NMR) yield of **3d**: IR (CCl_4) 2187, 1339, 1156 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 4H), 7.48 (s, 4H), 7.38 (d, J = 8.4 Hz, 4H), 2.45 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 145.7, 138.3, 132.6, 130.1, 127.6, 120.9 (all Ph), 90.5 (*C*≡CS), 88.2 (C≡*C*S), 21.8 (CH_3); CI HRMS m/z 434.0649 M^+, calcd for $C_{24}H_{18}S_2O_4$ 434.0647.

Acknowledgment. We are grateful to the National Cancer Institute of the NIH (Grant 2RO1CA16903) for financial support.

Supplementary Material Available: Copies of ^1H NMR spectra for compounds **1h**, **3e**, **3h**, and **5** and ^{13}C NMR spectra for compounds **1h**, **3e**, and **3h** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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