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Efficient Preparation of *E*-β-Iodovinyl Phenylsulfone by Finkelstein Reaction at a Vinylic Center

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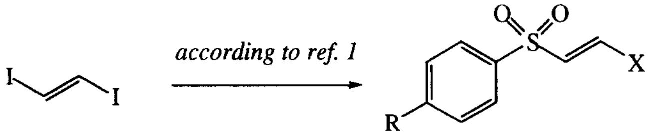
Abstract: Treatment of *E*-β-chlorovinyl phenylsulfone, a crystalline compound that can be conveniently prepared on a large scale from 1,1,2-trichloroethane, by sodium iodide in acetone at ca 130 °C, in a sealed vessel, affords the title iodosulfone in good yield.

In the course of an ongoing work aimed at studying the reactivity of various β-iodovinyl compounds with reducing species, we needed to prepare β-iodovinyl arylsulfones such as ***E*-1a** or ***E*-1b**. This was first attempted by treating, according to Russel,[1] *E*-1,2-diiodoethylene with mercuric benzenesulfinate in DMSO, under irradiation with a 275W Philips lamp. For unclear reasons, these conditions worked only erratically and though some sulfone ***E*-1a** could be obtained this way, the yield was only moderate (42%).



1a, R=H; X=I
1b, R=Me; X=I
1c, R=H; X=Cl

The inconsistency of these results, coupled with the necessity both to use a stoechiometric amount of mercuric compounds and to prepare the required diiodoethane, prompted us to apply to acetylene the iodosulfonylation conditions developed previously by Truce to prepare parent iodosulfones from 1-alkynes.[2]

Accordingly, an ethereal solution of tosyl iodide, preferred to the corresponding phenyl derivative owing to the better stability of the former, was stirred under an atmosphere of acetylene, the reaction mixture being illuminated as precedently. Not too surprisingly, given the very low solubility of acetylene in ether at the used temperature conditions (ca 20-25 °C), the expected addition proceeded very slowly and only trace amounts (ca 4%) of sulfone ***E*-1b** could be isolated after a few days. However, saturating at low temperature (ca -78 °C)

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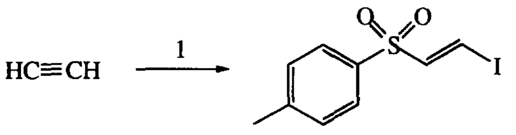
AcOEt with acetylene and stirring for a few days the resulting solution with tosyl iodide resulted in the formation of a 9/1 (NMR) mixture (54%) of, respectively, the sulfones **E-1b** and **Z-1b**, from which the pure *E* isomer could be isolated in an interesting 45% yield by recrystallization from CH_2Cl_2/hexane.[3]

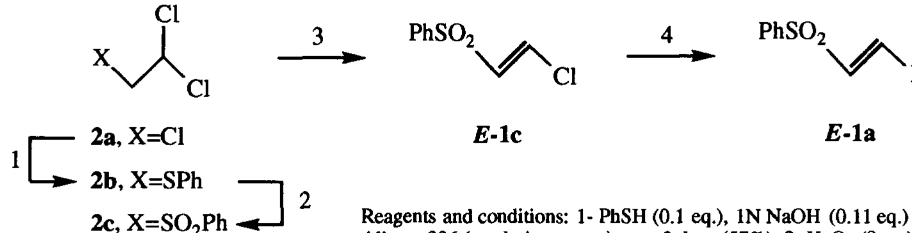


***E*-1b** M. p. 79-80 °C (Litt.[3b]: M. p. 79.6-80 °C)

Reagents and Conditions: 1- Tosyl iodide, AcOEt (see ref. 3a); - 78 °C to r. t., 5 days, then recrystallization from CH_2Cl_2/hexane (45%).

Even though a reasonable amount of the sulfone ***E*-1b** could thus be prepared, the hazards associated with the use of acetylene led us to examine an entirely different approach based on the nucleophilic displacement of the chlorine atom in the corresponding chlorosulfone ***E*-1c** by an iodide anion.

This chlorosulfone, whose preparation from the very cheap 1,1,2-trichloroethane **2a** has been described in literature,[4,5] is known to react with nucleophilic species to afford substitution products at the *β* position, presumably by an addition-elimination mechanism and, interestingly, with retention of configuration.[5] For instance, treatment of ***E*-1c** by a sodium alkoxide affords the corresponding *E*-2-alkoxyvinyl sulfone.[5a] Therefore, it could be hoped that ***E*-1c** would be converted into the iodosulfone ***E*-1a** by treatment with sodium iodide in acetone. This proved to be the case.

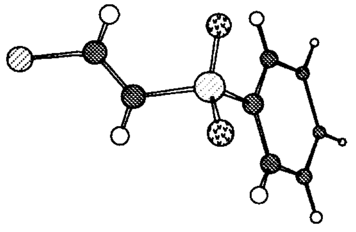


Reagents and conditions: 1- PhSH (0.1 eq.), 1N NaOH (0.11 eq.) , Aliquat 336 (catalytic amount); r. t., 3 days (57%); 2- H_2O_2 (8 eq.), ammonium molydate (0.1 eq.), MeOH; 0 °C to r. t., 14 hours (96%); 3- NEt_3 (1.1 eq.), CH_2Cl_2; 0 °C, 1 hour (87%); 4- NaI (5eq.), acetone; 135 °C, 1 day (76%).

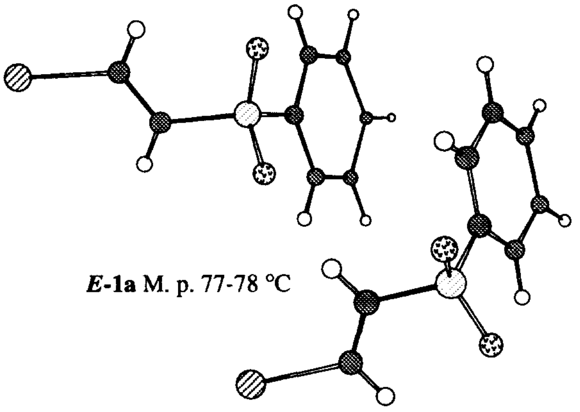
Preparation of the required sulfone ***E*-1c** was realised by modifying slightly the described procedure.[5a] Hence, treatment of **2a**, used both as a solvent and a reagent, by thiophenol and aqueous sodium hydroxide in phase-tranfer conditions afforded the bis-chlorosulfide **2b** (57% yield, after distillation). Oxidation of **2b** by hydrogen peroxide in the presence of a catalytic amount of ammonium molybdate then afforded the crystalline dichlorosulfone **2c** (96%), that, by treatment with triethylamine as described, afforded the desired chlorosulfone ***E*-1c** in good yield.

Prolonged treatment of this sulfone by excess sodium iodide in either acetone or 2-butanone at reflux proved disappointing, the starting sulfone remaining unchanged in these conditions. However, heating a solution of sulfone ***E*-1c** and NaI in acetone at 135 °C for 1 day, in a sealed vessel, resulted in the progressive formation of a white precipitate of NaCl and, after one day at that temperature, the pure sulfone ***E*-1a** could be isolated in a 76% yield.[6]

Although the NMR examination of both the starting and the resulting sulfones left little doubt on their structure,[7] confirmation of that assignment was obtained by performing an X-ray analysis of the monocrystals that formed by slow crystallisation of each sulfone **E-1a** and **E-1c** from diisopropyl ether.[8] As evidenced in the structures shown, generated from crystal data, both sulfones share the *E* configuration, which establishes unambiguously the stereoselectivity of this substitution process.



E-**1c** M. p. 51-52 °C



E-**1a** M. p. 77-78 °C

In conclusion, conditions for preparing *p*-tolylsulfone ***E*-1b** from acetylene by means of the Truce iodotosylation process have been defined. Additionally, a new, very convenient, procedure for the synthesis of the corresponding phenylsulfone ***E*-1a** on a large scale from the readily available trichloroethane **2a**, involving, in the key step, a Finkelstein substitution reaction at a vinylic center, has been contrived. Examination of the reactivity of these iodovinylsulfones with reducing metallic species is now being investigated. Results along this line will be published in due course.

Acknowledgements: Thanks are due to the Conseil Régional d'Alsace for a grant (to T. Z.).

Notes and References

1- Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. I.; Pla-Dalmau, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530-3538.

2- a) Truce, W. E.; Wolf, G. C. *J. Chem. Soc. Chem. Commun.* **1969**, 150; b) Truce, W. E.; Wolf, G. C. *J. Org. Chem.* **1971**, *36*, 1727-1732.

3- **Protocol for the iodosulfonylation of acetylene**: AcOEt (250 ml) was placed in a three-neck flask connected to a gasometer and to a bubbler, both *via* a stopcock, and to a Schlenck tube equipped with a sintered funnel containing tosyl iodide (23.53 g; 83.41 mmol). The whole apparatus was purged with argon and the flask was immersed in a cooling bath (dry-ice/acetone bath). Acetylene (washed successively by H_2O, H_2SO_4, and then dried on Na_2CO_3) was introduced *via* the gasometer until saturation (verified by weighting periodically the flask). AcOEt (80 ml) was added into the Schlenck tube with a serynge and the resulting solution of tosyl iodide was introduced dropwise, through the filter, into the flask whereas a slow stream of acetylene was maintained. The resulting mixture was gently stirred, and, without removing the bath, was allowed to reach slowly room temperature. The connection to the bubbler was then disrupted and the stirring was pursued, a weak pressure of acetylene being maintained constantly by means of the gasometer. After five days, the reaction mixture was poured into 10% (aqueous) sodium bisulfite (500 ml). The aqueous phase was extracted with ether (5x100 ml) and the pooled organic extracts were washed with sodium bisulfite (100 ml), and brine (2x50 ml), then dried ($MgSO_4$). The solid left by evaporation of the solvents was taken-up in CH_2Cl_2 (minimum amount), after that hexane was added. After one day, the crystals were collected and washed with a cold, 1/1, hexane/diisopropyl ether mixture (2x10 ml) to give the pure sulfone *E*-**1b** (10.38 g; M. p. 79-80 °C). By evaporating the solvents, the mother liquor gave a solid product that was chromatographed on silica gel (hexane/AcOEt) to give, successively, additionnal sulfone ***E*-1b** (2.31 g; total yield 45%) and the isomeric sulfone **Z-1b** (1.29 g; M. p. 195-196 °C). Attempted use of the two-phase (*i.e.* H_2O/AcOEt) modification of the Truce procedure, with *in situ* generation of tosyl iodide from sodium *p*-tolylsulfinate and iodine, as described by Inomata[3b] proved not so rewarding, the sulfone ***E*-1b** being then isolated in a yield not exceeding 15%; b) Iwata, N.; Morioka, T.; Kobayashi, T.; Asada, T.; Kinoshita, H; Inomata, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1379-1388. Physical data (M. p., NMR) consonant with the values we recorded are given for compound ***E*-1b**, but no indication is provided concerning either the used protocol or the yield.

4- McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Tetrahedron Lett.* **1985**, *26*, 6301-6304.

5- a) Pelter, A.; Ward, R.; Litle, G. M. *J. Chem. Soc. Perkin I* **1990**, 2775-2790; b) Farina, V.; Hauck, S. I. *J. Org. Chem.* **1991**, *56*, 4317-4319.

6- **Protocol for the 1c-1a conversion**: A solution of sulfone ***E*-1c** (2.5 g; 12.38 mmol) and dry NaI (9.25 g; 61.68 mmol) in anhydrous acetone (50 ml) was prepared in a tube, then thoroughly degassed (three "freeze and thaw" cycles). While its content was still frozen (liquid nitrogen), and under a reduced pressure of argon, the tube was sealed and placed in a autoclave, half-filled with acetone, that was subsequently closed and immersed for 24 hours in an oil bath maintained at 135 °C. After cooling (liquid nitrogen), the tube was opened. The formed white precipitate, identified to NaCl, was separated by filtration and the colourless filtrate was evaporated. The solid residue thus left was taken up in CH_2Cl_2 (250 ml). and the resulting, clear, solution was washed with saturated $NaHCO_3$ (30 ml), 10% sodium bisulfite (30 ml), and brine (2x30 ml), then dried ($MgSO_4$), and filtered on silica gel (CH_2Cl_2). The solvents were evaporated and the resulting white solid was recrystallized from diisopropyl ether to afford the pure sulfone ***E*-1a** (2.77g; 76%) as colourless crystals (M. p. 77-78 °C).

7- **Selected data: *E*-1a**: ^{1}H NMR: 7.29 (d, J=14.5 Hz, 1H); 7.53-7.72 (m, 3H); 7.53-7.72 (m, 3H); 7.88-7.91 (m, 2H); 8.03 (d, J=14.5 Hz, 1H); ^{13}C NMR: 96.1, 127.9, 129.6, 134, 139, 143.5; **Z-1b**: M. p. 195-196 °C; ^{1}H NMR: 2.42 (s, 3H), 7.3-7.37 (m, 2H), 7.43 (d, J=4 Hz, 1H), 7.59 (d, J=9 Hz, 1H), 7.84-7.89 (m, 2H); ^{13}C NMR: 21.8, 93.4, 128.3, 130, 136.9, 141, 145.3. ^{1}H and ^{13}C NMR at 200 and 50 MHz, respectively, in $CDCl_3$. The results presented herein are taken in part from the doctorat dissertation of T. Z. (Strasbourg, 1998).

8- **Crystal data for *E*-1a** (colorless crystal of dimensions 0.40x0.40x0.40 mm^3): $C_8H_7O_2SCl$, M= 202.66, monoclinic, space group P 2_1/c, a= 8.3854 (6), b= 10.4624 (8), c= 11.2922 (6), β= 107.030 (5) °, V= 947.2 (2) Å^3, Z= 4, d_{calcd}= 1.42 gcm^{-3}, μ(MoKα)= 0.569 mm^{-1}. A total of 2126 reflections was collected, 2.5<θ<26.29 °. 1139 reflections having I>3σ(I). Absorption factors: 0.89/1.00. 109 parameters. Final results: R(F)= 0.045, Rw(F)= 0.066, GOF= 1.325, maximum residual electronic density= 0.45 eÅ^{-3}. **Crystal data for *E*-1c** (yellow crystal of dimensions 0.30x0.30x0.30 mm^3): $C_{16}H_{14}O_4S_2I_2$, M= 588.22, orthorhombic, space group Pna2_1, a= 15.202 (2), b= 8.218 (1), c= 16.128 (2) Å, V= 2014.9 (2) Å^3, Z= 4, d_{calcd}= 1.94 gcm^{-3}, μ(MoKα)= 3.302 mm^{-1}. A total of 2364 reflections, 2.5<θ<26.29 °. 1578 reflections having I>3σ(I). Absorption factors: 0.78/1.00. 216 parameters. Final results: R(F)= 0.034, Rw(F)= 0.048, GOF= 1.032, maximum residual electronic density= 0.41 eÅ^{-3}. The absolute structure was determined by refining Flack's x parameter.

In common: room temperature, Nonius MACH3 diffractometer and MoKα graphite monochromated radiation (λ= 0.71073 Å), step-scan. The structures were solved using direct methods and refined against |F|. Hydrogen atoms were introduced as fixed contributors. Empirical absorption corrections derived from psi scans. For all computations the Nonius OpenMoleN package (OpenMoleN, Interactive Structure Solution, Nonius B.V., Delft, The Nederlands (1997)) was used. Further details of the crystal structure investigation are available on request from the Director of Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EW (U.K.), on quoting the full journal citation.