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# HYPERVALENT IODINE IN SYNTHESIS: 9. A NEW, EFFECTIVE SYNTHESIS OF ACETYLENIC SULFONES

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Alkynylphenyliodonium salts can easily react with sodium sulfinates under PTC conditions at room temperature to afford a convenient, effective method for the preparation of acetylenic sulfones.

Acetylenic sulfones are well-known very important synthetic intermediates. They not only represent an interesting class of dienophiles in view of the various reaction modes which can be predicted the basis of their unusual way of addition to unsaturated substrates, for example, (4+2)-cycloaddition,[1] (2+2)-cycloaddition,[2] 1,3-dipolar cycloaddition,[3] fragmentation-addition,[4] but also can take free radical chain substitution reaction with $RHgCl$ $R_2Hg$,[5] and they also can react with organolithium or organomagnesium reagents to give higher acetylenes.[6]

According to the importance of acetylenic sulfones in organic synthesis, there are many methods available for their synthesis including oxidization of acetylenic thio ethers,[7] eliminaion of β-haloalkenyl sulfones,[8] reaction of substituted acetylenes with mercury(II) chloride and sodium benzensulphinate followed by oxidative demercuriation,[9] diazotization of the corresponding 5-aminoisoxazoles,[10] reaction of 2- oxoalkylphenyl sulfones with diethyl chlorophosphate followed by elimination,[11] and the reaction of 1,2-bistrimethylsilyl acetylene with benzensulfonyl chloride followed by treatment with potassium carbonate.[12]

However these methods are deficient in some respects, such as low yields, expensive, toxic or not readily available reagent, strict reaction conditions or difficulties with isolation of the product and limited scope. It is necessary to develop a new, effective method for the synthesis of acetylenic sulfones.

There is considerable current interest and research activity in tricoordinate iodine(III)compouds.[13] The latest members of the family of multicoordinate iodine species, alkynylphenyliodonium salts(1), have become valuable reagents in organic synthesis. They

$$PhI^{+}—C\equiv C-R\ X^{-}$$

(1)

serve as precursors to the first examples of alkynyl tosylates,[14] alkynyl carboxylates,[15] and alkynyl[15a-16] phosphates and for the preparation of conjugated enynes by the treatment of (1) with vinylcopper reagents[17], for the synthesis of alkyne carboxylates by the alkoxycarbonylation of (1).[18] The photochemical production of alkynylphosphonium salts form (1) ($X=BF_4$) with triphenylphonsphine has also been described.[19] Azide ion[20] and β-dicarbonyl anion[21] add to (1) in Michael fashion.(1) also function as alkynylation agents in both organic[22] and organometallic[23] chemistry. In the course of our studies on the hypervalent iodine in synthesis, coupled with the ready availability and high reactivity of (1),

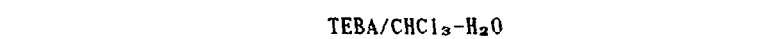
Table (1). Acetylenic sulfones (3) prepared

| Product | Reaction Time(min) | Yield (%) | m.p.(°C) | Molecular Formula[c] or Lit.m.p. | $^1$H-NMR, ppm ($CDCl_3$/TMS) | IR(KBr) $cm^{-1}$ |
|---|---|---|---|---|---|---|
| 3a | 5 | 75[a] | 70-72 | 73-74[7a] | 7.33-7.78(m,8H)<br>8.00-8.21(m,2H) | 2180,1590,<br>1450,1340,<br>1168,1085,<br>760, 683. |
| 3b | 10 | 81[a] | 47-48.5 | $C_{12}H_{14}O_2S$<br>(222.3) | 1.23 (s,9H)<br>7.47-7.37(m,3H)<br>7.87-8.10(m,2H) | 2900,2212,<br>2179,1335,<br>1165,1089,<br>755, 685. |
| 3c | 5 | 68[a] | 82-83 | 83-84[8b] | 2.50(s,3H)<br>7.30-7.67(m,7H)<br>7.87-8.10(d,2H) | 2180,1603,<br>1450,1362,<br>1156,1087,<br>815,760,680 |
| 3d | 10 | 72[a] | 100 | 99.5-100.5[8b] | 1.29(s,9H)<br>2.51(s,3H)<br>7.25-7.50(d,2H)<br>7.78-8.00(d,2H) | 2990,2210,<br>2180,1342,<br>1152,1089,<br>818,780 |
| 3e | 2 | 88[b] 74[a] | 104-105 | $C_{14}H_9ClO_2S$<br>(276.7) | 7.43-7.81(m,7H)<br>7.96-8.07(d,2H) | 2180,1450,<br>1338,1160,<br>1089,1011,<br>830,755,705. |
| 3f | 5 | 92[b] 80[a] | 80-82 | $C_{12}H_{13}ClO_2S$<br>(256.7) | 1.25(s,9H)<br>7.48-7.59(d,2H)<br>7.88-7.99(d,2H) | 2996,2208,<br>2175,1590,<br>1342,1160,<br>1090,1010,<br>836,780,752. |
| 3g | 5 | 89[b] 77[a] | 67-69 | $C_{14}H_9NO_4S$<br>(287.3) | 7.45-7.83(m,6H)<br>8.30-8.91(m,3H) | 2180,1540,<br>1358,1338,<br>1170,1125,<br>880,760,750. |
| 3h | 10 | 95[b] 84[a] | 111-112 | $C_{12}H_{13}NO_4S$<br>(267.3) | 1.25(s,9H)<br>7.80-8.92(m,4H) | 2990,2210,<br>2178,1540,<br>1354,1338,<br>1168,1123,<br>880,814,788. |

a: Yield of isolated analytically pure product (recrystalliztion), based on (1). b: Purity 99% by G.L.C.

c: Satisfactory microanalyses obtained:
C±0.29; H±0.15; N±0.20.

prompted us to examine their reaction with sodium sulfinates. Such reaction would provide an effective route to acetylenic sulfones. Herein we report our result, an effective method for the synthesis of acetylenic sulfones (3) by direct S- alkynylation of sodium sulfinates (2) with alkynylphenyliodonium salts ( 1) . Simple stirring of the alkynylphenyliodonium salts (1) with the sodium sulfinates (2) in two phase system of chloroform and water in the presence of catalytic amount of TEBA at room temperature gave after workup and isolation the desired products, acetylenic sulfones ( 3), in good yield as given Table (1).




(1) (2) (3)

| R= | R′= | | R | R′ |
|---|---|---|---|---|
| Ph- | Ph- | a | Ph- | Ph- |
| t-Bu- | P-$CH_3C_6H_4$ | b | t-Bu- | Ph- |
| | P-$CLC_6H_4$ | c | Ph- | P-$CH_3C_6H_4$ |
| | m-$NO_2C_6H_4$ | d | t-Bu- | P-$CH_3C_6H_4$ |
| | | e | Ph- | P-$CLC_6H_4$ |
| | | f | t-Bu- | P-$CLC_6H_4$ |
| | | g | Ph- | m-$NO_2C_6H_4$ |
| | | h | t-Bu- | m-$NO_2C_6H_4$ |

The products were characterized by spectral and comparison of experimental values with literature values as summarized in the Table(1).

This reaction represents a new, efficient method for the direct synthesis of acetylenic sulfones (3). It has some advantages over the existing ones such as accessible starting materials, mild reaction conditions, simplicity of the procedure and better yields. Furthermore, the range of useful applications of alkynylphenyliodon

-ium salts as alkynylating agents in organic chemistry has been extended.

General procedure for the preparations of acetylenic sulfones (3); A solution of alkynylphenyliodonium salt (1) 2mmol in 10ml $CHCl_3$ was added to solution of sodium sulfinate (2) 2.5mmol and 0.1mmol TEBA in 10ml $H_2O$, then the mixture was stirred at room temperature for the time as given in Table (1).After the reaction was complete, the organic layer was separated, and the water layer was extracted with $CHCl_3$(3×10ml).The combined organic layers were washed with water (3×20ml) and dired over anhydrous $MgSO_4$ .After removal of the solvent,the residue was recrystallized from hexane or was chromatographed on silica gel using 2:1 hexane/dichloromethane as eluent to afford the acetylenic sulfone (3).All relevant data are summarized in Table(1).

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