Notes

Preparation and Photodecomposition of α-Toluenesulfonyl Iodide

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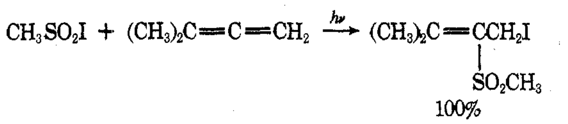
We have recently studied the light-initiated addition of sulfonyl iodides to various allenes and have reported[1,2] that both alkyl- and arylsulfonyl iodides will add to various allenes to give 1:1 adducts. When substituted allenes such as phenylallene or 3-methyl-1,2-butadiene were employed, nearly quantitative yields of the 1:1 adducts resulting from attack by an intermediate sulfonyl radical on the central carbon of the allenic unit were usually obtained. For example, methanesulfonyl iodide would combine very rapidly (within 1–2 min) with 3-methyl-1,2-butadiene under the influence of light to give a quantitative yield of 1-iodo-2-methanesulfonyl-3-methyl-2-butene.



$$CH_3SO_2I + (CH_3)_2C{=}C{=}CH_2 \xrightarrow{h\nu} (CH_3)_2C{=}C(SO_2CH_3)CH_2I \quad 100\%$$

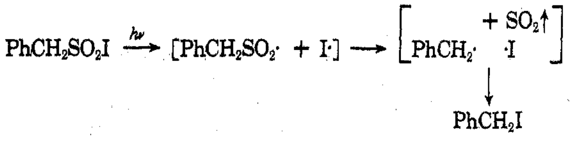
The alkylsulfonyl iodides in this work were not isolated, but were used as freshly prepared benzene solutions owing to the instability of these compounds. Thus, when a benzene solution of iodine was vigorously mixed with an aqueous solution containing an excess of the appropriate sodium alkylsulfinate, the intense purple color of the iodine rapidly faded and was replaced by the bright yellow-orange color of the sulfonyl iodide. When no further color change was evident, the benzene layer was separated, dried briefly over $MgSO_4$, and filtered to give a clear yellow-orange solution of the sulfonyl iodide. Delay in using this dried solution or exposure to strong light produced considerable decomposition of the sulfonyl iodide; hence the solutions were used immediately and were protected from the light until the allene was present. Yields were generally based on starting iodine; from the results quoted it is apparent that the alkylsulfonyl iodides themselves are produced in quantitative or nearly quantitative yields. This technique, used by Truce and Wolf,[3] in the addition of sulfonyl iodides to acetylenes as well as in our work with allenes, has proved to be an extremely useful method of generating and handling unstable sulfonyl iodides.

Since relatively little is known of the chemistry of sulfonyl iodides and few have been prepared owing to their instability, we have attempted to prepare several novel sulfonyl iodides by utilizing the procedure previously described.

Results and Discussion

α-Toluenesulfonyl iodide was successfully generated in benzene solution, but was not isolated. An attempt was made to add this freshly prepared sulfonyl iodide to 3-methyl-1,2-butadiene. Accordingly, a slight excess of 3-methyl-1,2-butadiene was added to a dry benzene solution of the sulfonyl iodide and the solution was exposed to illumination from a 240-W General Electric sun lamp. The color quickly faded and the solution became colorless. Removal of solvent under vacuum gave an 89.4% yield of benzyl iodide, which was pure by nmr. The infrared spectrum of the crude material contained no sulfone bands, and, more importantly, the nmr spectrum of the crude material showed only the presence of benzyl iodide; none of the 3-methyl-1,2-butadiene was involved in this reaction.

This transformation is rather remarkable, in that apparently the intermediate sulfonyl radical is either extruding sulfur dioxide rapidly and the resulting benzyl radical recombining with the iodine atom within the solvent cage, according to the following scheme



$$PhCH_2SO_2I \xrightarrow{h\nu} [PhCH_2SO_2\cdot + I\cdot] \longrightarrow \left[\begin{matrix} & + SO_2\uparrow \\ PhCH_2\cdot & \cdot I \end{matrix}\right] \longrightarrow PhCH_2I$$

or the benzyl iodide is being formed *via* the following chain reaction.

$$PhCH_2SO_2I \xrightarrow{h\nu} PhCH_2SO_2\cdot + I\cdot$$

$$PhCH_2SO_2\cdot \longrightarrow PhCH_2\cdot + SO_2$$

$$PhCH_2\cdot + PhCH_2SO_2I \longrightarrow PhCH_2I + PhCH_2SO_2\cdot$$

We favor the cage mechanism as being somewhat more likely owing to the complete lack of any products involving the allene, although with the information at hand we cannot rigorously distinguish between these mechanisms.

The stability of the benzylic radical provides a driving force for extrusion of sulfur dioxide from the sulfonyl radical, and in fact the carbon–sulfur bond dissociation energy for the process

$$PhCH_2SO_2\cdot \longrightarrow PhCH_2\cdot + SO_2$$

has been calculated at 7.5 kcal/mol,[4] an extraordinarily low value for a bond dissociation energy. Thus it is reasonable that the $PhCH_2SO_2\cdot$ radical should extrude sulfur dioxide very rapidly. A similar extrusion of sulfur dioxide from α-toluenesulfonyl chloride has been observed under radical conditions.[5]

The properties of trichloromethanesulfonyl iodide would be interesting, since the sulfonyl radical would be a particularly polar one owing to the presence of three chlorine atoms. However, all of our attempts to prepare trichloromethanesulfonyl iodide failed. Similar results were obtained in attempts to prepare chloromethanesulfonyl iodide.

The bond strength of the sulfur–iodine bond would appear to be too weak in these two sulfonyl iodides to provide any driving force for the formation of the desired sulfonyl iodide. Indeed, it has been reported[6] that trichloromethanesulfonyl chloride is readily reduced and liberates iodine from an aqueous potassium iodide solution, a point which was readily verified in these laboratories. Studies on the equilibrium constant for formation of the sulfonyl iodides in aqueous solution have shown that the equilibrium constant is very sensitive toward electronegative substituents in the sodium sulfinate.[7] Thus, for the reaction

$$RSO_2^- + I_3^- \rightleftharpoons RSO_2I + 2I^-$$

$$K = \frac{[RSO_2I][I^-]^2}{[RSO_2^-][I_3^-]}$$

where R = C_6H_5, K was calculated as 1×10^{-2}, but, when R = 2,5-dichlorophenyl, K was calculated as 4×10^{-7},[7] a difference of over 10^6. In the light of these data, the failure to prepare trichloromethanesulfonyl iodide and chloromethanesulfonyl iodide is not surprising.

Because of the greater stability of the arylsulfonyl iodides (which usually permits their isolation) the preparation of various arylsulfonyl iodides containing an electronegative substituent on the aromatic ring should be possible. We have indeed found that *p*-nitrobenzenesulfonyl iodide can be prepared in the same manner as *p*-toluenesulfonyl iodide,[1,8] by combining an aqueous solution of the sulfinate with an ethanolic solution of iodine. This sulfonyl iodide was found to slowly evolve iodine vapors at room temperature and appeared to be about as stable as *p*-toluenesulfonyl iodide.

Experimental Section

All melting points are uncorrected. Nmr spectra were recorded on a Varian A-60A and ir spectra were recorded on a Beckman IR-33. The nmr spectral data are reported in chemical shift from TMS (δ 0), with s, d, t, q, and m referring to singlet, doublet, triplet, quartet, and multiplet, respectively. Microanalyses were performed by Dr. C. S. Yeh and staff of this department. The α toluenesulfonyl chloride was purchased from Eastman and the 3-methyl-1,2-butadiene was obtained from Chemical Samples Co.

Preparation of Sodium Trichloromethanesulfinate. Trichloromethanesulfonyl chloride (20.5 g, 0.10 mol) was treated with sodium sulfite (25.2 g, 0.20 mol) and sodium bicarbonate (16.8 g, 0.20 mol) in water at 40–45° to give 20.5 g (85.4%) of the sulfinate, ir strong absorption at 790, 1040, and 1085 cm^{-1}. *Anal.* Calcd for CCl_3NaO_2S: Cl, 51.77; Na, 11.19. Found: Cl, 51.63; Na, 11.30. The sulfinate was found to decompose slowly in air. If the reaction temperature was raised to 90°, the yield and purity were greatly reduced.

Preparation of Sodium *p*-Nitrobenzenesulfinate. *p*-Nitrobenzenesulfonyl chloride (22.16 g, 0.10 mol) was treated with sodium sulfite (25.2 g, 0.20 mol) and sodium bicarbonate (16.8 g, 0.20 mol) in approximately 100 ml of water at 75–95° to give 5.0 g (24%) of sodium *p*-nitrobenzenesulfinate: mp 232–233° dec; ir 1510 and 1350 cm^{-1} ($-NO_2$); nmr (D_2O, TMS external standard) δ 7.83 (q).

Preparation of α-Toluenesulfonyl Iodide and Attempted Addition to 3-Methyl-1,2-butadiene. Treatment of α-toluenesulfonyl chloride (38.13 g, 0.20 mol) with sodium sulfite (50.4 g, 0.40 mol) and sodium bicarbonate (33.6 g, 0.40 mol) in 200 ml of water afforded 25.1 g (70.5%) of white solid sulfinate which after a few minutes of exposure to air began to fume and to liberate heat. The material was quickly transferred to a vacuum desiccator and subsequently protected from the air. The nmr spectrum of this product (D_2O, TMS external standard) showed that purity of this material was now not greater than 50%. Because of the apparent instability of the sodium α-toluenesulfinate, the salt was not isolated, but was used as a freshly prepared aqueous solution. Thus, α-toluenesulfonyl chloride was treated with 1 equiv of sodium sulfite and sodium bicarbonate in water at 70–75° and the resulting crude aqueous solution was used without further purification in the following preparation of α-toluenesulfonyl iodide. The α-toluenesulfonyl iodide was generated by vigorously mixing the freshly prepared aqueous solution of sodium α-toluenesulfinate (0.025 mol) with a benzene solution of iodine (5.08 g, 0.02 mol, in *ca.* 200 ml of benzene). The bright yellow benzene solution was separated and dried, then used immediately in the following reaction.

The benzene solution of α-toluenesulfonyl iodide (0.02 mol in *ca.* 200 ml of benzene) was treated with 3-methyl-1,2-butadiene (1.5 g, 0.221 mol). Upon illumination from a 250-W General Electric sun lamp, the bright yellow color rapidly faded and the solution became colorless. Evaporation of the solvent under vacuum gave 3.9 g (89.4%) of benzyl iodide, nmr ($CDCl_3$) δ 4.23 (s, 2), 7.0–7.33 (m, 5). The infrared spectrum of this material contained no sulfone bands, and the nmr spectrum of this material showed only the presence of benzyl iodide; no adducts between 3-methyl-1,2-butadiene and α-toluenesulfonyl iodide could be detected. Further proof of the product identification was obtained as follows.

Treatment of benzyl chloride (1.26 g, 0.01 mol) with sodium iodide (6.0 g, 0.04 mol) in acetone according to the procedure of Coleman and Hauser[9] yielded 1.75 g (80.3%) of benzyl iodide. The benzyl iodide prepared in this manner was compared by ir and nmr and found to be identical with the material produced in the above reaction from α-toluenesulfonyl iodide.

Treatment of the product (1.09 g, 0.005 mol) with sodium benzenesulfinate (1.64 g, 0.01 mol) in methanol at room temperature yielded 1.1 g (94.8%) of the known[10] benzyl phenyl sulfone: mp 149–150° (lit.[5] mp 148°); nmr ($CDCl_3$) δ 4.28 (s, 2), 6.90–7.77 (m, 10).

Preparation of *p*-Nitrobenzenesulfonyl Iodide. When an aqueous solution of sodium *p*-nitrobenzenesulfinate (0.52 g, 0.0025 mol) was treated with a solution of iodine (0.635 g, 0.0025 mol) in ethanol, a yellow solid rapidly precipitated from solution. The solid was collected and recrystallized from CCl_4 to give 0.4 g (51.1%) of *p*-nitrobenzenesulfonyl iodide: mp 96–100° dec; nmr ($CDCl_3$) δ 8.28 (q). The product was found to slowly evolve iodine at room temperature, but was more stable at −10°. The sulfonyl iodide was particularly unstable in chloroform solution.

Attempted Preparation of Trichloromethanesulfonyl Iodide. Treatment of a benzene solution of iodine (0.254 g, 0.001 mol) with an aqueous solution of sodium trichloromethanesulfinate (0.41 g, 0.002 mol) produced no visible reaction. Use of iodine monochloride in place of iodine in the above procedure also failed to produce the sulfonyl iodide (as evidenced by no visible color change) even when a large excess of the sulfinate was employed.

Attempted Preparation of Chloromethanesulfonyl Iodide. Treatment of chloromethanesulfonyl chloride (7.45 g, 0.05 mol) with sodium sulfite (6.3 g, 0.05 mol) and sodium bicarbonate (8.4 g, 0.10 mol) in water at 50–55° yielded 4.1 g (60.2%) of crude sulfinate of approximately 88% purity (by nmr), nmr (D_2O, TMS external standard) δ 4.10 (s), impurity δ 6.07 (s). The impurity is believed to be sodium dichloromethanesulfinate derived from dichloromethanesulfonyl chloride believed to be present in the starting material. Repeated distillation, however, was ineffective in purifying the starting chloromethanesulfonyl chloride. Recrystallization from ethanol was ineffective in purifying the sodium chloromethanesulfinate, thus the sulfinate was used in this purity in the following attempts to prepare chloromethanesulfonyl iodide. The sulfonyl iodide could not be produced by treating an aqueous solution of excess sulfinate with either a solution of iodine in benzene or a solution of iodine monochloride in benzene. In neither case was the dark color (of the iodine or iodine monochloride) discharged.

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Registry No. Sodium trichloromethanesulfinate, 42521-49-3; trichloromethanesulfonyl chloride, 2547-61-7; sodium p-nitrobenzenesulfinate, 15959-31-6; *p*-nitrobenzenesulfonyl chloride, 98-74-8; α-toluenesulfonyl iodide, 42880-77-3; 3-methyl-1,2-butadiene, 598-25-4; benzyl iodide, 620-05-3; *p*-nitrobenzenesulfonyl iodide, 42880-78-4; chloromethanesulfonyl chloride, 3518-65-8; sodium chloromethanesulfinate, 42880-79-5.

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The Crystal Structure of *cis*-2,4-Diphenylthietane *trans*-1-Monoxide[1]

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Dodson, Jancis, and Klose have studied the unusual stereochemistry of small heterocyclic rings containing sul-