Addition Reactions and Stability of Arylsulfonyl Thiocyanates

S. CARROCK OLSEN and
C. CHRISTOPHERSEN*

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Due to our standing interest in thiocyanates derived from organic acids,[1,2] our attention was drawn to a communication by Goerdeler and Rosenthal [3] describing the synthesis and some reactions of sulfonyl thiocyanates. A recent report by Wolf[4] confirming most of the findings of Goerdeler and Rosenthal now prompts us to report some aspects of the addition of *p*-tolylsulfonyl, *1*, and *p*-chlorophenylsulfonyl thiocyanate, *2*, to the carbon-carbon double bond and the stability of these thiocyanates. Apparently the two papers mentioned [3,4] and two patents [5,6] are the only information available on organic sulfonyl thiocyanates.**

Addition reactions to the carbon-carbon double bond. Addition of *1* to styrene gives rise to 2-phenyl-2-thiocyanatoethyl *p*-totylsulfone, *3*.[3,4] Using the method of Goerdeler *et al.*[3] we have confirmed this result and found the styrene adduct of *2* to be analogous to *3*.

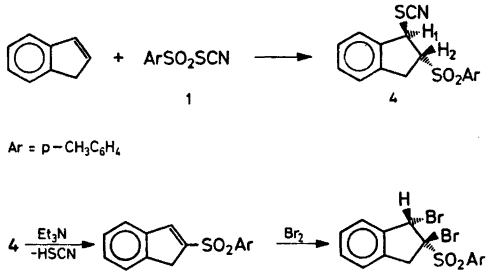
As decribed by Wolf, *3* on treatment with triethylamine undergoes a facile *trans* elimination of thiocyanic acid from the most stable conformation. We have confirmed this result and found analogous behaviour for the adduct of *2* thus giving rise to *trans*-2-phenyl-1-(arylsulfonyl)ethylene ($J = 15-16$ Hz for the alkene protons which is well within the limits reported for *trans* alkene protons, $J = 11-19$ Hz[10]).

To secure the stereochemistry of the addition reaction *1* and *2* were added to acenaphthylene and indene. By ^{1}H NMR analysis of the reaction mixture the addition reactions proved to be stereospecific.

The product from the addition of *1* to acenaphthylene exhibits two doublets at $\delta = 5.22$ and $\delta = 5.40$, $J \approx 2$ Hz, which is the value expected for *trans* coupling, while J (*cis*) $\sim 6-7$ Hz.[11-13] The corresponding values for additions of *2* were $\delta = 5.33$, $\delta = 5.48$ and $J \approx 2$ Hz securing the *trans* configuration for this product as well. The possibility of the formation of isothiocyanate derivatives was excluded by inspection of the IR spectra, which showed the characteristic SCN stretching vibration at 2160 cm^{-1}.

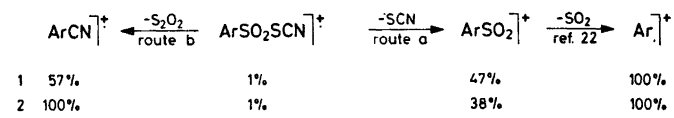
By analysis of the spin-spin coupling pattern from the ^{1}H NMR spectrum of *3* it was evident that the arylsulfonyl group exerts a more pronounced deshielding effect than does the thiocyanate group, meaning that the geminal protons adjacent to the sulfonyl group appear at higher field than the one adjacent to the thiocyanate group. Bearing this in mind, the ^{1}H NMR spectrum of the addition product of *1* and indene, exhibiting a doublet at $\delta(H_1) = 4.98$, $J_{1,2} = 4$ Hz and a multiplet around $\delta(H_2) = 4.0$, strongly support the formulation of this product as 1-thiocyanato-2-(*p*-tosyl) indane *4*. The elimination of thiocyanic acid from *4* proved much more difficult than in the case of *3*, and the ^{1}H NMR spectrum of the resulting *p*-tosylindene did not distinguish between the two possible substitution patterns (*i.e.* the *p*-tosyl group in position 1 *versus* 2). However, addition of bromine gave rise to a product, the ^{1}H NMR spectrum of which exhibits a singlet at $\delta = 6.08$ and an AB pattern with doublets centered at $\delta = 3.64$ and $\delta = 4.28$ ($J_{AB} = 16.5$ Hz). These data are consistent with the formulation *4* but exclude the isomeric 2-thiocyanato-1-(*p*-tosyl)indane structure. The assignment of the *trans* configuration in *4* is partly based on the observed slow thiocyanic acid elimination, which according to this formulation has to be a *cis* elimination. Evidently, the coupling constants of the protons in the indane system are generally of little value in assigning stereostructures in this class of compounds.[14] The limits of the reported values are $J_{1,2}$ (*cis*) $\sim 4.4-8.5$ Hz and $J_{1,2}$ (*trans*) $\sim 1-7$ Hz.[14-17] However, the observed value in *4*, $J_{1,2} = 4.0$ Hz seems to be well below the smallest reported value for a *cis* relationship and is therefore in this case taken as substantial support for the assigned stereostructure of *4*.

Thermal and photochemical stability. We have observed that solutions of arylsulfonyl thiocyanates, when left at room temperature (23–24 °C) for extended periods of time, are



* To whom the correspondence should be addressed.

** According to Ashworth [7] arylsulfonyl thiocyanates might be formed from ethanolic solutions of arylsulfonyl chlorides and ammonium thiocyanates. The product of the reaction is described as a yellow amorphous precipitate, [7,8] insoluble in ethanol, ether, and benzene and melting higher than 230 °C.[9] Arysulfonyl thiocyanates have far lower melting points [3,4] therefore the products in question cannot be arylsulfonyl thiocyanates.



Scheme 1.

fairly stable. When a solution of *1* (5 % in CCl_4) was examined after 15 days a rough estimate based on the absorbance of the 2160 cm^{-1} and 1590 cm^{-1} bands showed that at least 90 % of the thiocyanate still remained. The same result was obtained for *2* under identical conditions (the estimate now based on the 2160 cm^{-1} and 1476 cm^{-1} bands).

During these experiments the IR spectra remained mainly unaltered except for a rather sharp absorption emerging at 1905 cm^{-1}. This band is highly characteristic of arylsulfonyl isothiocyanates.[18,19]

It is thus obvious that isomerization takes place to some extent, which is in contrast to an earlier statement by Goerdeler *et al.*[3] In thermolysis experiments at 146 °C ($Cl_2CHCHCl_2$, 12 h) compound *1* was still fairly stable, while *2* was extensively decomposed. Since arylsulfonyl isothiocyanates are thermally unstable[20,21] the possibility exists that the extensive decomposition may occur *via* the isomerization.

At irradiation with RUL 3000 Å lamps (Rayonet reactor, type RPR-208) at room temperature a fast isomerization to the corresponding arylsulfonyl isothiocyanates takes place. It is essential that the photolysis is carried out in deoxygenated solvents as a very fast photochemical reaction with oxygen was observed.

The mass spectra of sulfonyl thiocyanates are highly characteristic of this type of compound. Introduction of *1* and *2* through the direct insertion probe at 100 °C and 140 °C, respectively, gave rise to an utterly simple spectrum as shown in Scheme 1, route *a*.

Both *1* and *2* gave rise to low intensity peaks corresponding to loss of sulfur plus sulfur dioxide or S_2O_2 from the molecular ion. When the compounds were introduced through the gas inlet system (*1* at 120 °C and *2* at 140 °C) a drastic alteration in intensity distribution was noted. The compounds now degradate *via* both route *a* and *b*. In the case of *1* the intensity of the peak corresponding to loss of S_2O_2 from the molecular ion is second only to the base peak. In *2* this peak is base peak; the peak corresponding to ionized sulfur dioxide (*m/e* 64) also has gained intensity and is a major peak (80 %). These observations indicate thermal degradation reactions in the inlet system with loss of SO_2. This hypothesis was substantiated by the findings that reflux of solutions of *1* and *2* in 1,1,2,2-tetrachloroethane (b.p. 146 °C) for 12 h liberated 2.5 % and 7.9 %, respectively, of the theoretical amount of sulfur dioxide.

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