Treatment of tosylhydrazones with a commercial bleach solution rapidly reverted them in one step to the parent ketones, thereby confirming the validity of our proposal. The timing of the double extrusion (Cl^-, Ts^-) cannot be determined but it is immaterial from the synthetic standpoint.

Table I
Ketones from Tosylhydrazones

Ketone	Yield, %
Benzophenone	85
Acetophenone	69
Cyclohexanone	60
2-Methylcyclohexanone	63
Norcamphor	62

Acetophenone has been similarly obtained in reasonable yield, even though it is susceptible to further degradation (haloform reaction). Unfortunately the procedure is not very suitable for cleavage of aldehyde derivatives, since aldehydes were recovered in rather low yields, perhaps due to oxidation by hypochlorite.

Experimental Section

General Procedure for the Hydrolysis of Ketone Tosylhydrazones. The tosylhydrazone (1.0 g), dissolved or suspended in chloroform (30 ml), was shaken with 5% NaOCl (20 ml) for 5 min. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated. Distillation of the residue gave the ketone.

Registry No.—Benzophenone, 119-61-9; benzophenone tosylhydrazone, 4545-20-4; acetophenone, 98-86-2; acetophenone tosylhydrazone, 4545-21-5; cyclohexanone, 108-94-1; cyclohexanone tosylhydrazone, 4545-18-0; 2-methylcyclohexanone, 583-60-8; 2-methylcyclohexanone tosylhydrazone, 52826-41-2; norcamphor, 497-38-1; norcamphor tosylhydrazone, 38397-34-1.

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Communications

Sulfonyl Thiocyanates and Their Additions to Olefins, Acetylenes, and Allenes

Summary: Sulfonyl thiocyanates may be readily prepared from the appropriate sodium sulfinate and thiocyanogen; these new members of the sulfonyl halide/pseudohalide class react with unsaturated hydrocarbons to provide β-thiocyanatosulfones.

Sir: Investigations into the synthetic use of sulfonyl iodides (**2**, X = I)[1-3] coupled with the recent reports concerning the synthesis[4] and chemistry[5] of sulfonyl cyanides (**2**, X = CN) kindled our interest in the possible preparation of other sulfonyl pseudohalides. Perhaps the most facile method for preparing **2** is *via* the reaction of an aqueous solution of the sodium salt of the appropriate sulfinic acid (**1**) with molecular iodine (X = Y = I), or with cyanogen chloride (X = CN; Y = Cl). Considering the similar reactivities of molecular iodine and thiocyanogen,[6] it was felt the generation of **2** (X = SCN) was a rational goal.[7]

$$\underset{\mathbf{1}}{ArSO_2^-Na^+} + XY \longrightarrow \underset{\mathbf{2}}{ArSO_2X} + NaY$$

The finding that thiocyanogen is relatively stable as a benzene solution in contact with water[8] (at least at temperatures below 10°) provided the opportunity for attempting the synthesis of *p*-toluenesulfonyl thiocyanate in a manner similar to that employed for the analogous cyanide[4b] and iodide.[2]

A clear, pale yellow benzene solution of **2** (X = SCN) was obtained on mixing a cold, aqueous solution of sodium *p*-toluenesulfinate with a benzene solution of thiocyanogen. Similarly, solutions of the methyl and ethyl homologs were prepared. In practice the sulfonyl thiocyanate could be used in this form or, with the aryl derivative, it could be isolated (64%) as a crystalline solid. *p*-Toluenesulfonyl thiocyanate is a moderately stable, white solid, mp 37–39°, which undergoes only slow decomposition when refrigerated. Decomposition is obvious after 1 month as noted by a dark yellow color and the odor of sulfur dioxide. At elevated temperatures this process is accelerated. Confirmation of the structure was provided by elemental analysis, and nmr, ir, and mass spectral data (see supplementary pages). Supporting this structure is the known reactions of thiocyanogen with various nucleophiles invariably providing the corresponding thiocyanate. In addition, *p*-toluenesulfonyl thiocyanate, on standing in absolute ethanol for 24 hr at room temperature, provided a virtually quantitative yield of ethyl *p*-toluenesulfonate.

Table I
Reactions of Sulfonyl Thiocyanates with Unsaturated Hydrocarbons

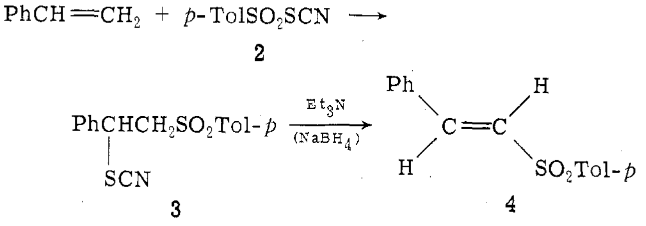
Reaction	RSO_2-SCN, R	Unsaturated hydrocarbon	% yield of isolated adduct	Mp, °C, of adduct
1	*p*-Tol	Styrene	43	112–112.5
2	*p*-Tol	Cyclohexene	84	90–92
3	Me	Cyclohexene	57	89–91
4	*p*-Tol	Phenylethyne	79	111–112
5	*p*-Tol	Cyclohexylethyne	68	116–117
6	*p*-Tol	3-Hexyne	5	70–72
7	Me	3-Hexyne	13	53–55
8	Et	Cyclohexene	35	71–72
9	*p*-Tol	3-Methyl-1,2-butadiene	53	99–100
10	Me	3-Methyl-1,2-butadiene	12	66–67

Bacon, *et al.*, have shown that arylalkyl hydrocarbons may undergo homolytic thiocyanation with either thiocyanogen or thiocyanogen chloride.[9] It has also been noted that sulfonyl iodides (but not sulfonyl cyanides) undergo a very facile free-radical addition to unsaturated hydrocarbons.[2] Under more rigorous conditions, sulfonyl cyanides react with olefins, but not with acetylenes.[5] It has now been found that combination of a sulfonyl thiocyanate (aryl or alkyl) and an unsaturated hydrocarbon (olefin, acetylene, or allene) provides a fair to good yield of a product giving the correct elemental analysis for a 1:1 adduct. That this material is a thiocyanate rather than an isothiocyanate was confirmed by the ir spectrum. Thus, all adducts in Table I showed a very strong, sharp band between 4.64 and 4.67 μ. Isothiocyanates are known to absorb at longer wavelength—4.67–5.26 μ—and these bands are usually broad.[10] We have been unable to detect any appreciable amount of isothiocyanate (by ir) in any of the crude reaction mixtures.[11]

That the reactions are homolytic in quality is supported by the nature of the adducts obtained which are analogous to those obtained in the known free-radical additions of sulfonyl iodides. Consistent also is the fact that large quantities of polystyrene were obtained in the reaction of methanesulfonyl thiocyanate with styrene. The biting odor of sulfur dioxide was noted during the reactions in which alkanesulfonyl thiocyanates were employed; this observation is consistent with the intermediacy of $RSO_2\cdot$, which decomposes to $R\cdot$ and SO_2.

The yields listed in Table I have not been optimized though it has been found that these additions require a large excess of hydrocarbon for best results. Thus, in reaction 2, as the molar ratio of cyclohexene was increased in the manner 1:1, 2:1, 4:1, and 10:1, the corresponding yields of isolated product were 15, 38, 53, and 84%. The yields given in Table I are the result of hydrocarbon excesses ranging from 2:1 to 10:1.

Careful monitoring of several of the reactions (1–4, 9) by both tlc and glpc methods has revealed, in addition to starting materials and very slow moving components (most certainly polymeric in nature) no more than 10% minor products with R_f values and retention times comparable with those of the isolated adducts.



That structure 3 correctly represents the adduct obtained in the p-toluenesulfonyl thiocyanate addition to styrene was confirmed by its further, facile conversion to 4 (93%). Based on the known trans additions of sulfonyl iodides, it seems reasonable to assign structures resulting from trans addition of the sulfonyl and thiocyanato moieties in reactions 2–8; however, this matter is currently under investigation.

The spectral data of the adducts from reactions 9 and 10 confirm that addition has occurred to the less substituted double bond. The nmr spectrum of the adduct from reaction 10 shows three unequal methyl groups as singlets, in addition to a methylene group (singlet). With 9, one of the methyl groups is replaced by a p-tolyl function. That the thiocyanato group was attached to the terminal carbon was determined by the interesting borohydride conversion of this latter adduct to 2-(p-toluenesulfonyl)-3-methylbut-1-ene in 57% yield. Similar borohydride treatment of 3 provided 4 in 88% yield.

Though the chemistry of these 1:1 adduts may, in some respects, resemble that found when sulfonyl iodides are employed, the presence of the thiocyanato moiety in the current compounds provides an unusually reactive functionality which should be subject to the known transformation of thiocyanates,[6] thereby providing access to numerous unique β-substituted sulfones.

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Supplementary Material Available. A full experimental section describing the synthesis of all adducts in Table I, as well as the preparation of **4, 6,** and p-toluenesulfonyl thiocyanate will appear following these pages in the microfilm edition of this volume of the journal. Additionally, full nmr, ir, and analytical data are tabulated. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3454.

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(11) The possibility of obtaining isothiocyanates was validly raised by one of the reviewers; we have found, and intend to report in detail later, that indeed some of our adducts may be readily isomerized to the corresponding isothiocyanates.

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Condensation of *tert*-Butyl α-Lithioisobutyrate with Acid Chlorides. A Synthesis for β-Keto Acids and Ketones

Summary: The acylation of *tert*-butyl α-lithioisobutyrate with benzoyl chlorides gives the corresponding β-keto esters in good yield, and subsequent treatment of these esters with trifluoroacetic acid either at room temperature or at reflux affords β-keto acids or isobutyrophenones, respectively.

Sir: Recently dianions of carboxylic acids[1] and *O*-silyl ketene acetals[2] have been used to prepare β-keto acids and β-keto esters, respectively. However, the former method does not work well for the preparation of α-benzoyl carboxylic acids and the latter method is inapplicable to the synthesis of α,α-disubstituted β-keto esters. Herein we report a new procedure[3] for the facile synthesis of both of these classes of compounds and for their conversion into the corresponding ketones.

Treatment of *tert*-butyl α-lithioisobutyrate with benzoyl chlorides (**1**) gave the *tert*-butyl α-benzoylisobutyrates[4] (**2**) in fair to good yields.[5] The *tert*-butyl esters **2** upon treatment with trifluoroacetic acid for 15 min at room temperature afforded the β-keto acids[6] **3** in quantitative yield. The corresponding ketones **4** can be readily prepared, essentially quantitatively, by heating solutions of **2** in trifluoroacetic acid under reflux for 1 hr.