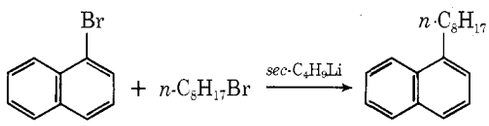
1:5 mixture of hexane and diethyl ether yields only 3% of 1 over the same period at the same temperature.

As summarized in Table I, a wide variety of aryl halides react readily with primary alkyllithiums to produce the cross-coupled products in high yields. On the other hand, secondary and tertiary alkyllithiums do not give the cross-coupled products in any appreciable yields under the comparable conditions. These results suggest that the actual coupling step involves the interaction of aryllithiums with alkyl halides formed by the halogen–metal exchange reaction. Indeed, phenyllithium prepared from bromobenzene and lithium metal reacted with *n*-octyl bromide in the presence of THF to produce *n*-octylbenzene in 87% yield within 2 hr at room temperature. Based on these results we have developed the following convenient procedure involving the use of a hindered alkyllithium, *i.e.*, *sec*-butyllithium. 1-Bromonaphthalene was treated sequentially with equimolar quantities of *sec*-butyllithium and *n*-octyl bromide to provide 1-*n*-octylnaphthalene (**2**) in 74% yield (eq 3). Only trace quantities of 1-*sec*-butylnaphthalene and 3-



(3)

2

methylundecane were present. The benzyne mechanism[4] does not appear significant, since no 2-naphthyl derivatives were detected.

It should be noted that any of the three procedures described here provides a convenient alternative to the Wurtz–Fittig route for the coupling of aryl halides with alkyl halides.

Experimental Section

The following examples are representative of the three procedures discussed in this report.[5]

Preparation of 1-*n*-Butylnaphthalene by the Reaction of 1-Bromonaphthalene with *n*-Butyllithium (Procedure I). To a dry 100-ml flask equipped with a magnetic stirring bar, a septum inlet, and an outlet connected to a mercury bubbler were introduced sequentially 20 ml of THF, 2.07 g (1.41 ml, 10 mmol) of 1-bromonaphthalene, and 4.30 ml (11 mmol) of 2.56 *M* *n*-butyllithium in hexane while controlling the reaction temperature at 25 ± 5°. After stirring the mixture for 2 hr, it was washed with water and aqueous sodium chloride. The combined aqueous layer was extracted with chloroform and the combined organic layer was dried over magnesium sulfate, evaporated, and distilled to yield 1.21 g (66% yield) of 1-*n*-butylnaphthalene: bp 78–80° (0.05 mm); n^{25}D 1.5807 [lit.[6] bp 289°; n^{20}D 1.5819]; pmr (CCl_4, TMS) δ 0.8–2.0 (m, 7 H), 3.00 (t, 2 H, *J* = 7.5 Hz), 7.2–8.1 (m, 7 H) ppm; ir (neat) 797, 785 (sh), 775 cm^{-1}.

Preparation of *n*-Octylbenzene by the Reaction of Phenyllithium with *n*-Octyl Bromide (Procedure II). In a setup similar to that described above 5.56 ml (10 mmol) of 1.80 *M* phenyllithium in a 70:30 mixture of benzene and diethyl ether and 2.12 g (1.89 ml, 11 mmol) of *n*-octyl bromide in 20 ml of THF were reacted at 25 ± 5° for 2 hr. The mixture was worked up in a manner analogous to that described above to give 1.56 g (82%) of *n*-octylbenzene: bp 82–85° (0.5 mm); n^{25}D 1.4832 [lit.[7] bp 131–134° (12 mm); n^{20}D 1.4851]; pmr (CCl_4, TMS) δ 0.7–1.9 (m, 15 H), 2.58 (t, 2 H, *J* = 7.5 Hz), 7.12 (s, 5 H) ppm; ir (neat) 745, 695 cm^{-1}.

Preparation of 1-*n*-Octylnaphthalene by the Coupling of 1-Bromonaphthalene and *n*-Octyl Bromide under the Influence of *sec*-Butyllithium (Procedure III). In a setup similar to that described above 2.07 g (1.41 ml, 10 mmol) of 1-bromonaphthalene in 10 ml of diethyl ether was treated at room temperature with 13.7 ml (11 mmol) of 0.80 *M* *sec*-butyllithium in hexane. After stirring the mixture for 10 min 2.12 g (1.89 ml, 11 mmol) of *n*-octyl bromide and 10 ml of THF were added in this order at 25 ± 5°. The mixture was stirred for 3 hr and then worked up as described above to yield 1.59 g (66%) of 1-*n*-octylnaphthalene: bp 120–123° (0.05 mm); n^{24}D 1.5515 [lit.[8] bp 144.5° (0.2 mm); n^{20}D 1.5533]; pmr (CCl_4, TMS) δ 0.7–2.0 (m, 15 H), 3.01 (t, 2 H, *J* = 7.5 Hz), 7.2–8.1 (m, 7 H) ppm; ir (neat) 797, 788, 776 cm^{-1}.

Acknowledgment. We thank Research Corporation and Syracuse University for financial support.

References and Notes

(1) R. G. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951).
(2) The marked rate-accelerating effect of THF in the aryl-alkyl coupling reaction producing the cross-coupled products in high yields does not appear to have been clearly documented.[1,3]
(3) A rate-accelerating effect of THF in certain aryl–aryl coupling reactions has been reported: H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 447 (1957). These reactions almost certainly proceed *via* the benzyne mechanism. In a report describing the reaction of alkyl or aryl halides with lithium metal in THF, the same authors [H. Gilman and B. J. Zaj, *J. Org. Chem.*, **22**, 1165 (1957)] made the following observations: (1) the yields of alkyl- or aryllithiums decrease in the order Cl > Br > I, (2) the higher the reaction temperature, the lower the yields were. These results were rationalized in terms of the rate-accelerating effect of THF in the alkyl–alkyl or aryl–aryl coupling. However, no product study was made.
(4) See, for example, G. Wittig, *Angew. Chem., Int. Ed. Engl.*, **4**, 731 (1965).
(5) All reactions were carried out under a nitrogen atmosphere with precautions to exclude air and moisture. Diethyl ether and THF were purified by distillation from lithium aluminum hydride. The pmr spectra were obtained using a Varian A-60 nmr spectrometer.
(6) G. Harris, J. R. A. Pollock, and R. Stevens Ed., "Dictionary of Organic Compounds," Oxford University Press, New York, N.Y., 1965.
(7) R. C. Weast Ed., "Handbook of Chemistry and Physics," 52nd ed, The Chemical Rubber Co., Cleveland, Ohio, 1971.
(8) B. Barrowsmith, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 2072 (1965).
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Regeneration of Ketones from Tosylhydrazones

Tse-Lok Ho* and Chiu Ming Wong

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada

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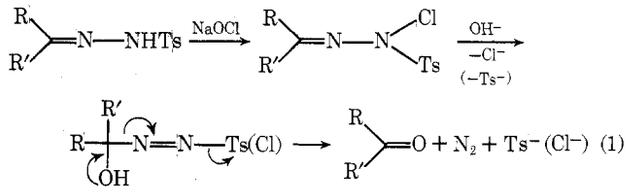
Tosylhydrazones serve as intermediates for the synthesis of olefins[1] and the creation of carbenes.[2] Those derived from α,β-epoxy ketones undergo fragmentation readily to afford acetylenic carbonyl compounds.[3] Generally, tosylhydrazones are highly crystalline, therefore they should be valuable for the characterization and purification of carbonyl substances. However, this last potential utility and also their applicability as protective device have been virtually completely ignored, presumably owing to their high hydrolytic stability.

Thus the recovery of carbonyl compounds from tosylhydrazones represents a pragmatic problem yet to be resolved. During the regenerative process, a hydroxyl group is to be attached to the imino carbon, and, to augment the electrophilicity of this center toward water or hydroxide ion, an additional electron-withdrawing, good leaving group has to be temporarily introduced to the tosyl-bearing nitrogen. According to our plan, such an operation is in fact mandatory, because a combination of an S_N2' displacement and then a fragmentation is required for the ultimate generation of the carbonyl and the release of molecular nitrogen. Further elaboration of this scheme indicated that the most elegant and convenient way to effect the overall transformation would be the reaction with alkali hypochlorite (eq 1). This reagent furnishes both Cl^+ for N-chlorination and OH^- for deprotonation and the nucleophilic attack.



(1)

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.

References and Notes

(1) R. H. Shapiro and M. J. Heath, *J. Amer. Chem. Soc.*, **89**, 5734 (1967).
(2) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **81**, 5513 (1959); **83**, 3159 (1961).
(3) A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, **50**, 708 (1967); J. Schreiber, *et al.*, *ibid.*, **50**, 2101 (1967).

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 reac-

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

tivities of molecular iodine and thiocyanogen,[6] it was felt the generation of **2** (X = SCN) was a rational goal.[7]

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