

riety of functional groups.¹ Alkynes are most often prepared by dehydrogenation of *vic*- and *gem*-dihalogeno compounds and halogeno vinyl derivatives with strong base.¹ The decomposition of *p*-toluenesulfonylhydrazones of carbonyl compounds possessing a leaving group such as mesyloxy, acetoxy, halogeno,² and epoxy group³ at the α position have been used for preparation of alkynes. Pyrolysis of 5-chloromethyl-1*H*-tetrazole⁴ was also treated as a unique method for synthesis of alkynes. We have investigated a new synthetic design for formation of carbon-carbon triple bond by the use of carboxylic acid and (methylthio)methylithium derivatives as two carbon units of the triple bond as outlined in Scheme 1. We describe the results of the study in this paper.

Reaction of benzoic acid with 2.5 equiv of (methylthio)benzylithium⁵ (2 ; $R^2 = C_6H_5$) afforded phenyl (methylthio)benzyl ketone **3a**, whose *p*-toluenesulfonylhydrazone **4a** was treated with methylithium in dry Et₂O to give diphenylacetylene **5a**⁶ in 65% yield.⁷ Treatment of lithium 3,4-dimethoxybenzoate **1b**⁸ with (methylthio)methylithium⁹ (2 , $R^2 = H$) in dry THF gave 3,4-dimethoxyphenyl (methylthio)methyl ketone **3b** in 93% yield. *p*-Toluenesulfonylhydrazone **4b**, derived from **3b**, was treated with methylithium in dry Et₂O with stirring to afford 3,4-dimethoxyphenylacetylene **5b**¹⁰ in 95% yield. In this way, lithium phenylpropionate **1c**, lithium *n*-nonanoate **1d**, lithium *n*-decanoate **1e** and lithium cyclohexylcarboxylate **1f** were converted to 4-phenyl-1-butyne **5c**,¹¹ 1-decyne **5d**,¹¹ 1-undecyne **5e**,¹² and cyclohexylacetylene **5f**.¹³ Furthermore, *n*-butyllithium was also found to be useful for synthesis of alkynes from *p*-toluenesulfonylhydrazone of α -methylsulfenylated ketones. *p*-Toluenesulfonylhydrazone **4e** was treated with *n*-butyllithium in dry THF in the presence of TMEDA to give 1-undecyne in 80% yield.¹⁴

This new method for preparation of alkynes starting from carboxylic acid should be applicable for formation of a variety of alkynes.

Experimental Section

All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were dried and distilled from LiAlH₄ before use. Nuclear magnetic resonance spectra were recorded on a Varian T-60 instrument and mass spectra were determined on a Hitachi RMU-7L instrument.

General Procedure for Preparation of α -Methylsulfenylated Ketones (3) from Lithium Carboxylate (1). To a suspension of lithium carboxylate **1** (13.7 mmol), prepared from the carboxylic acid and an equimolar amount of *n*-BuLi in THF at 0 °C, was added a solution of (methylthio)methylithium⁹ (20.5 mmol) in THF at 0 °C. After stirring at 0 °C for 0.5 h and then at room temperature for 14 h, the mixture was poured into water and extracted with benzene. The extract was washed with water, dried over Na₂SO₄, and evaporated to leave **3** in 90–95% yield. For the preparation of **3a**, benzoic acid was treated with (methylthio)benzylithium (2.5 equiv) in THF at –78 °C under stirring. The mixture was maintained at the same temperature for 0.5 h and then at room temperature for 14 h. The mixture was worked up as above to give **3a** in 70% yield. The crude ketones thus obtained were used for preparation of *p*-toluenesulfonylhydrazones **4** without purification.

General Procedure for Preparation of *p*-Toluenesulfonylhydrazones (4). A mixture of **3**, an equimolar amount of *p*-toluenesulfonylhydrazide, and EtOH was refluxed for 3 h except in the case of **3a** and **3b**. For the preparation of **4a** and **4b**, the mixture was heated for 30 h under reflux. Evaporation of the solvent gave **4** as colorless needles in 85–95% yield.¹⁵

General Procedure for Preparation of Alkynes (5). (a) To a stirred suspension of **4** (6 mmol) in Et₂O (40 mL) was added an ethereal solution of MeLi (36 mmol) at 0 °C. After 0.5 h at 0 °C and then 30 h at room temperature with stirring, the mixture was poured into water and extracted with Et₂O. The extract was washed with water, dried over Na₂SO₄, and evaporated to leave **5**. (b) To a stirred suspension of **4** (6.5 mmol) in THF (40 mL) containing TMEDA (19.5 mmol) was added *n*-BuLi (hexane solution, 19.5 mmol) at –78 °C. After stirring had been continued at 0 °C for 0.5 h and then at room temperature for 24 h, the mixture was worked up as above to give **5**. By this method 1-undecyne (**5e**) was obtained in 80% yield.

Registry No.—*p*-Toluenesulfonyl hydrazide, 1576-35-8.

References and Notes

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- All *p*-toluenesulfonylhydrazones gave satisfactory analyses.

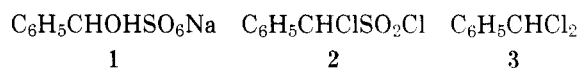
Conversion of Aromatic and α,β -Unsaturated Aldehydes to Dichlorides by Thionyl Chloride and Dimethylformamide¹

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In an attempt to convert the bisulfite addition product of benzaldehyde **1** to the corresponding dichloro compound, **2**, by treatment with thionyl chloride in the presence of dimethylformamide (DMF)³ we found that benzal chloride, **3**, was formed in high yield. This reaction was studied because it was hoped to be of value in converting substituted benz[*a*]anthracenes into corresponding dichlorides.



Further study revealed that treatment of benzaldehyde with thionyl chloride in the presence of a catalytic amount of DMF yielded **3** almost quantitatively at room temperature. Without DMF no reaction occurred.^{4,5} The generality of this reaction with aromatic and α,β -unsaturated aldehydes was demonstrated with 1-naphthaldehyde **6** (91% yield), cinnamaldehyde **7** (90%), and α -methylcinnamaldehyde **8** (85% only about 75% of which was (*E*)-1,1-dichloro-2-methyl-3-phenyl-2-propene). Slightly smaller yields were obtained with the corresponding bisulfite addition compounds of **6**, **7**, and **8**. However, since aldehydes are often isolated and/or purified by means of their bisulfite addition compounds, the conversion of the latter to the dichloro compounds could save a step without overall loss of yield. In the case of *n*-octanal, cyclohexanone, and acetophenone, such mixtures of products were obtained that this reaction was of no utility.

When equal moles of DMF and SOCl₂ are mixed in the cold in CH₂Cl₂ and the solvent is removed under vacuum a colorless solid, **4**, remains for which the ionic structures **4a** and **4b** have been advanced^{6–8} largely because of the slight solubility in nonpolar solvents. If this complex is heated SO₂ is lost and **5** is formed. Heating of DMF with PCl₅, COCl₂, oxalyl chlo-